MEASUREMENT AND PREDICTION OF HERBICIDE TRANSPORT INTO SHALLOW GROUNDWATER

By

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DEDICATION

To my mother,

Corrine L. Smith

She was taken from her family by illness during this research. Her wisdom, courage, and strength continue to inspire me. Without that inner strength, I would never have made it this far.

I love you Mom.

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MEASUREMENT AND PREDICTION OF HERBICIDE
TRANSPORT INTO SHALLOW GROUNDWATER

By

Matthew Clay Smith

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A field study was conducted to observe the movement of the herbicides atrazine and alachlor within the soil profile and a shallow water table aquifer following a surface application. Surface-applied bromide was used as a nonadsorbed tracer of water movement. The movement of nitrate from a fertilizer application to the site was also monitored. Measurements of chemical concentration were made using soil core samples, samples of soil water from the unsaturated zone, and water samples from monitoring wells below the water table.

Atrazine was observed to move rapidly with both saturated and unsaturated flows. Concentrations of atrazine exceeded 350 μg/L in soil water samples at a depth of 61 cm. Samples of shallow groundwater contained atrazine residues as high as 90 μg/L. Measurable concentrations of alachlor did not move below a depth of 45 cm in the soil.

Bromide and nitrate concentrations in soil water demonstrated large variability between sampling locations. Nitrate concentrations in the groundwater exceeded 40 mg/L after fertilization of the field.

Two root/vadose zone pesticide transport models, GLEAMS and PRZM, were used to simulate the conditions on the site. Comparisons were made between model simulation results and observed data. The uncalibrated models predicted concentrations that were generally within an order of magnitude, and often were within a factor of 2 to 3, of observed values. Differences between the predictions of the models appear to be due to the relative detail by which each model describes soil properties as a function of depth.

CHAPTER 1
INTRODUCTION

Agricultural production systems have undergone many changes since the 1940s. The capability of post-war industry to synthesize almost unlimited varieties of chemicals in great quantities has provided farmers with an arsenal with which to battle insects, weeds, and disease. These chemicals can also provide plants with required nutrients and regulate their growth. The result of using these chemical tools along with improved machines for planting, cultivating, and harvesting has been a dramatic increase in the productivity of the American farmer.

However, some serious problems associated with the use of agricultural chemicals have been identified in recent years. Many of these chemicals are toxic to non-target organisms such as birds, fish, and the person who is applying them. Rachel Carson (1962) brought to the attention of the public the potential harmful effects of using these chemicals in large quantities over large land areas. Since the publication of her book 'Silent Spring' there has been much research conducted to evaluate the fate of agricultural chemicals in the environment. During the 1960s and 1970s, great effort was initiated to determine the quantities of soil, fertilizers and pesticides which were entering our lakes and rivers. Through these efforts methods have been

developed (though only a few have been implemented) to minimize or eliminate agricultural impacts on surface waters.

The discovery of abandoned waste sites such as the famous Love Canal and the discovery of the pesticide aldicarb in the shallow groundwater on Long Island in New York generated concern for the protection of groundwater. These concerns led to analyzing samples of groundwater for toxic wastes and pesticides.

As more groundwater samples were analyzed, it became apparent that agricultural chemicals had somehow entered groundwater aquifers in several areas of the country. These results were publicized, and citizens throughout the nation expressed alarm that they were drinking potentially toxic chemicals. The federal and state governments responded to these concerns by intensifying monitoring efforts and reviewing data on the many agricultural chemicals to determine potential for leaching to groundwater and the extent of the current problem. Several federal agencies, along with university and private industry scientists, began developing computer models to help explain why these chemicals were moving beyond their target locations and to screen chemicals for their relative mobilities in soil. A limiting factor in the development and utilization of these models was a lack of the detailed data needed to test and validate model predictions.

To date, data on the presence of agricultural chemicals in groundwater have been limited primarily to sampling of municipal and domestic wells, providing only a large scale picture of contamination. There have been only a few intensive monitoring studies completed which provide sufficient data for model parameter estimation. Currently, there

are increased efforts at specific sites to provide more detailed monitoring of chemical movement through the soil profile and within groundwater aquifers.

The study described here is an effort to develop data for use in the development and testing of models which describe the fate and transport of pesticides and nutrients used in agriculture.

CHAPTER 2
OBJECTIVES

The overall objective of this research is to develop data on the movement of two widely used herbicides through the crop root zone, through the vadose zone (unsaturated zone between the crop root zone and the top of the unconfined water table aquifer), and within the shallow water table aquifer. These data will then be compared with the predictions of two root/vadose zone pesticide transport models.

The specific objectives are to perform the following:

1. Instrument a field site for monitoring the movement of water and chemicals through the soil profile and a shallow, water table aquifer.
2. Observe the fate and transport of surface-applied herbicides (atrazine and alachlor) over time.
3. Use surface-applied bromide as a nonadsorbed tracer of water movement.
4. Observe transport of the nitrate component of fertilizers applied to field.
5. Compile the observations of chemical movement into a data base for use in testing pesticide transport models.
6. Simulate the field conditions present during the monitored period with two pesticide transport models and compare to observed results.

CHAPTER 3
REVIEW OF THE LITERATURE

3.1 Evidence of Pesticide Residues in Groundwater

The U. S. Environmental Protection Agency estimates that at least 19 pesticides have been detected in groundwater in 24 states as a result of agricultural practices (U.S. EPA, 1987a). The total number of pesticides detected in groundwater is greater than nineteen. These additional detections are the result of manufacturing, storage, and loading activities which are not included in the above figures. The number of reported cases of pesticides in groundwater is increasing. Cohen et al. (1986) suggest that the increase is due to improvements in the quality and quantity of studies instead of an increase in the problem.

The insecticide/nematicide aldicarb was detected in the shallow groundwater on Long Island, New York in 1979 (Wartenburg, 1988). Aldicarb was used as an insecticide on potatoes. Aldicarb was detected in 20 of 31 wells tested in 1978 and the presence was confirmed through a repeat sampling of the wells in June, 1979. According to the U.S. EPA (1987a), aldicarb residues have been detected in almost 2000 wells on Long Island. Concentrations of aldicarb exceeded the state health guideline of 7 μg/L (ppb) in nearly 50% of those wells. Concentrations as high as 515 μg/L were recorded in the Long Island wells as reported by Ritter (1986). Aldicarb residues have been found in groundwater in 15 states (Cohen et al., 1986) with typical concentrations reported in the range of 0.3 - 3 μg/L.

In the state of Florida, residues of the nematicide EDB have been detected in over 10% of the public and private drinking water wells which have been sampled (U.S. EPA, 1987a). Approximately 1,200 wells require treatment or have been closed as sources of drinking water. Marti et al. (1984) detected EDB in the groundwater in southwest Georgia. EDB residues have been detected in groundwater in at least 6 other states.

In California, residues of approximately 57 pesticides have been detected in groundwater (U.S. EPA, 1987a). Most of these detections were related to factors other than routine use on agricultural fields. The nematicide DBCP has been detected at levels exceeding 1 μg/L in approximately 60% of the 2500 drinking water wells tested.

Residues of the widely used herbicide atrazine are commonly identified in groundwater. Ritter (1986) reports that approximately 36,000,000 kg of atrazine were used in the United States in 1982. Atrazine has been detected in PA, IA, NE, WI, MN, and MD (U.S. EPA, 1987; Cohen et al., 1986; Ritter, 1986). According to Berteau and Spath (1986), atrazine has also been detected in concentrations of up to 2 μg/L in California groundwater. Pionke et al. (1988) reported atrazine concentrations in groundwater at levels up to 1.1 μg/L in an agricultural watershed in Pennsylvania. The wells sampled by Pionke et al. (1988) were all located in unconfined aquifers with depths to the water table ranging from 2 to 21 m. Atrazine concentrations of 10 μg/L have been reported in a karst aquifer in Iowa (Libra et al., 1986; Kelley et al., 1986).

Residues of the herbicide alachlor have been found in groundwater in the states listed for atrazine, excluding WI. According to Ritter

(1986), alachlor and atrazine together accounted for 25% of all pesticides sold in the U. S. in 1982. Ritter (1986) reported that in 1982, approximately 38,600,000 kg of alachlor were applied to cropland in the United States. Kelley et al. (1986) reported alachlor concentrations in groundwater as high as 16 $\mu g/L$ in Iowa.

There are many individual cases of pesticide residue detection in groundwater that could be cited. The reader is referred to the proceedings of the Agricultural Impacts on Groundwater Conferences (National Water Well Assoc., 1986, 1988) for a variety of reports concerning the detection of pesticide residues in groundwater. A book edited by Garner et al. (1986) is also a good source of information related to this subject.

3.2 Factors Which Influence Pesticide Transport To Groundwater

Donigian and Rao (1986a) list five processes which affect the fate and movement of chemicals within the soil. These processes are transport, sorption, transformation/degradation, volatilization, and plant uptake. Other authors, e.g., Cheng and Koskinen (1986), use slightly varied groupings which include the processes named above. The interactions of these processes over time and space determine the fate of chemicals in the soil. The spatial variability of soil properties and other factors is an important consideration when interpreting field data and model predictions (Donigian and Rao, 1986a). This section will describe each of the processes and some of the factors which influence or regulate them.

3.2.1 Transport

The chemicals can be transported in at least three different phases: adsorbed to solid materials, in solution, and as a vapor. Surface runoff can transport chemicals in both the adsorbed and solution phases. Erosion and transport of soil particles during rainfall and irrigation can result in significant transport of highly-adsorbed, low-solubility pesticides (Wauchope, 1978). For most pesticides, the majority of transport in runoff is in the solution phase (Wauchope, 1978; Rao and Davidson, 1980). Chemicals in the solution phase can be transported within the soil profile by saturated and unsaturated water flows.

Water percolating through the soil profile can transport chemicals in the solution phase beneath the root zone and possibly into groundwater. The most common methods used to describe the transport of water and solutes in porous media are based on the assumptions that Darcian flow conditions exist, and that solute movement is controlled by advective and dispersive processes (Freeze and Cherry, 1979; Jury, 1986a; Wagenet, 1986; Wang and Anderson, 1982). Darcian flow conditions imply that the flow equations are representative of some volume of soil. All soil properties such as pore size distribution and volumetric water content are assumed to be uniform throughout the volume of soil (Jury, 1986b).

The advective component of transport is usually based upon Richards' equation and describes the average rate of water flow. The average rate of solute flow is the product of the solute concentration and the average pore-water velocity. Additional transport of solute can occur due to mechanical mixing of water in adjoining pores during advective transport

and molecular diffusion of solute from pores with high concentrations to adjoining pores with lower concentrations (Freeze and Cherry, 1979). Molecular diffusion can be significant when average pore-water velocities are low; otherwise, the processes involved in mechanical dispersion usually dominate. Differences in pore-water velocities in the direction of bulk flow cause a spreading out, and consequently a lowering of peak concentrations, of the solute plume. Some of the solute will arrive at a reference point earlier, and some will arrive later, than would be predicted based upon the average linear flow velocity. This is referred to as longitudinal dispersion. The tortuosity and interconnection of pores in the soil will also cause the solute to move perpendicularly to the bulk flow direction. This is referred to as transverse dispersion. Freeze and Cherry (1979) and Rao et al. (1988) provide detailed discussions of the dispersive-diffusive processes and their mathematical formulations.

Transport predictions based upon the methods described above have not compared well with field observations, e.g. Jury et al. (1986). Numerous modifications to the general theory have been proposed in order to help explain and reduce the differences between field observations and theoretical predictions. Rao et al. (1980) proposed separating pore-water in soils into two regions: inter-aggregate and intra-aggregate. Convective-dispersive transport was assumed to be limited to the water in the inter-aggregate region. The intra-aggregate region was assumed to act as a source/sink of solute. Diffusion between the regions could remove or add solute to the water in the inter-aggregate region. Jury (1982) proposed a method of predicting the transport times of solutes to

specified depths which is not based on physical processes. Rather, the transfer function theory uses measured values to develop a probability density function of travel times and uses it to predict solute travel times to depths greater than those that were measured. Gish (1987) combined the convective-diffusive transport theory with a stochastic representation of water velocities to describe field-scale (average) concentrations of bromide at various depths in the soil profile. Comparisons between the average measured bromide concentrations and predicted values showed good agreement.

Volatilization from soil and plant surfaces transports the chemicals into the atmosphere and reduces the amount remaining for transport with runoff or percolation. Diffusion of chemicals in the vapor phase can also transport the chemical within the soil profile. Most transport models do not consider vapor diffusion.

Many of the factors which are assumed to influence the transport of chemicals through porous media are summarized by Jury (1986b). Some of the soil properties influencing transport are water content, bulk density, permeability, clay content, organic matter content, and water retention (field capacity). Helling and Gish (1986) present results of a simple modeling exercise to demonstrate the effect of several soil properties on pesticide transport. Some of the environmental factors which have been shown to influence transport are precipitation, evapotranspiration, and temperature (Jury, 1986b).

3.2.2 Sorption

The partitioning of solutes between the liquid and solid phases (dissolved and adsorbed) is a major factor determining the mass of

solute available for advective-dispersive transport through the soil profile. If the chemical of interest is strongly adsorbed, then only a small fraction will exist in the solution phase at a given time and be available for transport. Non-adsorbed chemicals, however, will exist entirely in the solution phase and are available for transport with percolating water.

Many pesticides are nonpolar and adsorption occurs primarily on organic matter surfaces. Pesticides and chemicals which are polar will adsorb primarily to clay surfaces (Jury, 1986c). Since the majority of pesticides are nonpolar, the adsorption onto soils has been primarily related to the organic matter or organic carbon content of the soil. A detailed discussion of the factors influencing pesticide adsorption onto soils is given by Jury (1986c). The relationship between concentrations of a pesticide in the dissolved and sorbed phases is often represented by the Freundlich equation:

$$S = KC^n \qquad 3.1$$

where S = adsorbed concentration ($\mu g/g$ of soil), C = solution concentration ($\mu g/mL$), and K and n are empirical constants for the soil-pesticide system. The exponent n in equation 3.1 is often assumed to be equal to 1.0 which results in a linear relationship of the form:

$$S = K_d C \qquad 3.2$$

where K_d = partition coefficient (mL/g of soil).

For most uses of equation 3.2 in transport modeling, the partitioning between the solution and adsorbed phases is assumed to be instantaneous and reversible. Errors associated with the assumptions of

linearity, instantaneous equilibrium, and reversibility are discussed by Rao and Davidson (1980).

The partition coefficient, K_d, is unique to a given pesticide-soil combination. However, Rao and Davidson (1980) report that investigators have shown that when K_d is normalized for the organic carbon content of the soil, the resulting value is independent of the soil type and can be considered a property of the pesticide. The normalized partition coefficient is represented as K_{oc} and is defined by:

$$K_{oc} = K_d * 100 / \%OC \qquad 3.3$$

where %OC is the percent organic carbon content of the soil and K_d is the measured partition coefficient. Methods for measurement of the partition coefficient are reviewed by Rao and Davidson (1980).

3.2.3 Volatilization

Volatilization of pesticides from the soil and plant surfaces reduces the amount of the pesticide available to be leached or transported with runoff. Volatilization also determines the quantity of the pesticide which exists in the vapor phase within the soil and thus the amount available for diffusive vapor transport. Thus, as noted by Donigian and Rao (1986a), volatilization affects both the fate and transport of a pesticide.

Some of the factors which influence volatilization are summarized by Jury and Valentine (1986). They are Henry's constant K_H, chemical concentration, adsorption site density, temperature, water content, wind speed, and water evaporation. Henry's constant, K_H is the ratio of saturated vapor density to solubility and is an index of the partitioning

between the vapor and solution phases. A larger K_H implies increased volatilization. Increasing concentrations of the pesticide will increase the volatilization as long as the vapor density is not saturated. Adsorption of the pesticide will reduce volatilization. Volatilization increases as temperature increases. As the soil water content decreases, the rate of volatilization increases. Increasing wind speed can increase the volatilization of pesticides, particularly those with low K_H values. Evaporation of water from the soil surface can transport pesticides from within the soil profile to the surface where temperature and wind effects can increase the volatilization. Each of these factors is discussed in more detail by Jury (1986d).

3.2.4 Transformation/degradation

Transformation of a pesticide is the change in structure or composition of the original compound and degradation is the breakdown of the compound into smaller fragments with eventual inorganic endproducts such as H_2O and CO_2 (Cheng and Koskinen, 1986). The transformation and degradation processes represent a loss of the original (or parent) compound, thus reducing the amount remaining in the soil for transport by surface runoff and percolation.

In general, transformation and degradation processes occur at faster rates on plant surfaces and in the top few centimeters of soil than in the deeper soil zones (Donigian and Rao, 1986a). Thus, a chemical that is foliar or surface-applied will likely degrade more rapidly than if it were incorporated. For non-persistent pesticides (half-lives less than 15-20 days), the timing of rainfall events or irrigation is important in

determining the fraction of the applied mass that will be available for transport. Events occurring shortly after application will likely result in the largest concentrations in runoff and percolation water (Wauchope, 1979; Donigian and Rao, 1986a). The timing of rainfall and irrigation events is less critical for persistent (half-lives in excess of 100 days) pesticides since they will reside in the soil for longer periods (Donigian and Rao, 1986a).

The major processes involved in transformation and degradation include biotransformation, chemical hydrolysis, photolysis, and oxidation-reduction (Donigian and Rao, 1986a). Factors influencing transformation and degradation of pesticides, as summarized by Jury and Valentine (1986), include: microbial populations, chemical concentration, temperature, oxygen, pH, soil water content, and light. Detailed descriptions of the many factors influencing these processes are presented by Rao and Davidson (1980), Valentine and Schnoor (1986), and Valentine (1986).

3.2.5 Plant processes

Plant processes relating to pesticides are very complex. The uptake, translocation, accumulation, and transformation of pesticides by plants affect the availability of pesticides for transport processes and the potential exposure to pesticide residues by the consumers of the vegetation, fruits, etc. (Donigian and Rao, 1986a). Plant processes can serve as both a sink and a source of pesticide residues available for transport.

Pesticides applied to plant foliage will likely be transformed or degraded more rapidly than if the pesticide were applied to the soil or incorporated. Pesticides on the foliage may also be absorbed into the plant. Pesticides in the solution phase may be taken up by plant roots and translocated to various parts of the plant. These processes serve as a loss mechanism reducing the availability of the pesticide for transport.

Pesticide residues on plant foliage can be dislodged by rainfall and irrigation and washed onto the soil surface, resulting in an increased mass of pesticide available for transport in runoff and percolation (Smith et al., 1981; Donigian and Rao, 1986a). Plant residues which are left on the soil surface or incorporated can also serve as a source of pesticide which may be available for transport.

3.3 Predicting Pesticide Transport

There are many methods that can be used to predict the mobility of a given pesticide. These range from simple indices to complex research models. Each method has value when used for the purpose for which it was designed and with recognition of the assumptions and limitations associated with it.

3.3.1 Indices of contamination potential

Rao et al. (1985) compared several methods for computing indices of the contamination potential of pesticides. Most of the indices are based on one or more chemical properties such as K_{oc} and solubility. Three indices also included distance to groundwater and recharge rate. The

attenuation factor (AF) proposed by Rao et al. (1985) can also be used to estimate the mass of pesticide which will leach below the root zone or out of the vadose zone and into groundwater. The AF index is the only one of the indices compared by Rao et al.(1985) which incorporated mass loadings.

Dean et al. (1984) developed a methodology in which soil characteristics, crop type, chemical properties, and management practices (e.g. tillage type) can be combined to find a cumulative frequency distribution of the percentage of applied pesticide mass leaching below the crop root zone. These frequency distributions were derived from hundreds of 25-year simulations of pesticide leaching using the PRZM model (Carsel et al., 1984). The methodology was applied to four crop types (corn, soybean, cotton, and wheat) and 19 representative growing regions. The results are somewhat unique in that the user is presented with a statistical probability of leaching based on a 25-year meteorologic record.

Another index which is currently receiving much attention is the DRASTIC index developed by Aller et al. (1985). This index does not consider chemical properties; instead, it is an index of the vulnerability of groundwater at a given location to contamination from surface-applied chemicals. The DRASTIC index assigns numerical scores or weights to seven factors which could influence pollution potential. The factors are depth to water, net recharge, aquifer media, soil media, topography, impact of vadose zone, and conductivity of the aquifer. The final DRASTIC score is used to describe an area as having high, medium, or low susceptibility to groundwater pollution.

DRASTIC has been used to map every county in the United States (Alexander and Little, 1986) as part of the first stage of a national survey of pesticide contamination of drinking water (U.S. EPA, 1987b). In the first county-level assessment the Southeast Coastal Plain, which covers all of Florida and southern Georgia, was shown to be the groundwater region of highest vulnerability.

Indices like those mentioned above are beneficial to regulatory agencies as a method to screen great numbers of compounds and locate vulnerable areas. This information can aid in allocating funding for further studies concentrating on the chemicals of interest in regions which may be most vulnerable. These studies may involve detailed modeling of pesticide transport to groundwater, modeling of surface and groundwater hydrology, and collection of data from test locations.

3.3.2 Transport models

There are many models of pesticide transport reported in the literature. These range from steady-state screening models, e.g. PESTAN (Enfield et al., 1982), to very complex process-oriented research models, e.g. LEACHMP (Wagenet and Hutson, 1986). Donigian and Rao (1986a), and Shoemaker and Magette (1987) review a number of the models which are available. Most models which are capable of simulating pesticide fate and transport do not explicitly represent agricultural management and cropping practice effects on runoff and leaching. Modifications of management practices will be one method of reducing pesticide leaching to groundwater. The models used for regulatory purposes should reflect the trade-offs between surface water and groundwater quality. There is some

evidence that no-till farming will increase pesticide transport to groundwater while reducing surface runoff and thereby reduce pollution of surface waters (Dick et al., 1986). Thus, solutions to one problem may exacerbate another problem. The models discussed below are capable of simulating, to some degree, agricultural management practice effects on pesticide fate and transport.

According to Donigian and Rao (1986a), SESOIL (The Seasonal Soil Compartment model) is designed for long-term simulation of pesticide fate in the soil environment. It was developed for the EPA and is used as a screening model. SESOIL can simulate many components of the hydrologic cycle including precipitation, evapotranspiration (ET) and surface runoff. The model considers transport within the unsaturated zone extending from the soil surface to the top of the saturated zone. The hydrologic responses are determined using physically based equations in which uncertainty has been included. The water balance used in the model is a statistical representation of the hydrologic components over a "season." A season is the time step of the model, e.g., month or year. Erosion is simulated using the Universal Soil Loss Equation (Wischmeier and Smith, 1978). Hetrick and Travis (1988) coupled SESOIL with EROS (a submodel of the CREAMS (Knisel, 1980) watershed model) to predict surface runoff and sediment yield from small watersheds. The pesticide component of the model considers most of the processes and factors influencing pesticide transport which were described in previous sections.

SESOIL requires calibration and represents long-term averages. Some of the results of use and testing of SESOIL reported by Donigian and Rao (1986a) indicate that it should not be used for short-term predictions.

The combined SESOIL/EROS model of Hetrick and Travis (1988) adequately predicted long-term (several months) average runoff and sediment yields when tested against data from three small watersheds. However, monthly predictions were not good, especially when most of the runoff occurred due to large single storm events.

MOUSE (Method Of Underground Solute Evaluation) was developed at Cornell University as a management model and a training tool for students and professionals (Steenhuis et al., 1987). MOUSE is an interactive, menu-driven program which can run on a IBM-PC or compatible computer. The model can read daily historical weather files or generate synthetic rainfall, air, and soil temperature patterns. Surface runoff is computed using the SCS curve number method. Erosion is not considered. Solute movement in the vadose zone considers advective and dispersive flux, as well as degradation and adsorption. MOUSE will also simulate the movement of a pesticide in a two-dimensional unconfined aquifer. Extensive graphics illustrate movement as it is being simulated.

PRZM (Pesticide Root Zone Model) is a field-scale hydrology and transport model developed by the EPA (Carsel et al., 1984). PRZM is a continuous model capable of simulating water and chemical fluxes over many years of historical daily weather records. Runoff is predicted based on the SCS curve number equation, and erosion is simulated using a modification of the Universal Soil Loss Equation for daily time steps. The model can simulate the entire vadose zone (soil surface to groundwater). The vadose zone can be characterized by several layers with varying properties. For calculations, the vadose zone is divided into many compartments of equal depth. The model simulates crop growth

(leaf area and rooting depth). Water in the root zone can be removed by percolation, evaporation, or transpiration by the plant. Percolation is calculated based on the water-holding capacity of the soil. When the water content in a layer exceeds field capacity (1/10 - 1/3 bar tension) the excess water drains into the next lower compartment. There is an option in PRZM that allows the draining of the profile to occur over a longer period than one day.

Pesticide processes represented include advective and dispersive flux, sorption, degradation in soil and on plant foliage, and plant uptake. Volatilization and transport in the vapor phase are not considered. Application of pesticides can be partitioned between the soil surface and plant foliage. Applications to the soil can be incorporated by tillage. Different degradation rates can be specified for soil and foliar pesticide residues. The degradation rate within the soil can also be varied by soil layer.

PRZM will simulate multiple applications of one pesticide each year for many years of continuous climatic record. Thus it can predict temporal variations in leaching and runoff. Effects of agricultural management and cropping practices can be simulated. PRZM allows the user to request time series results for many variables in the model. This feature is useful for observing processes at intermediate locations within the vadose zone over time.

GLEAMS (Groundwater Loading Effects of Agricultural Management Systems) is also a field-scale hydrology and transport model (Leonard et al., 1987). It is based upon the extensively documented and applied CREAMS model (Knisel, 1980). CREAMS is a nonpoint source model for

predicting sediment, nutrient, and pesticide losses with surface runoff from agricultural management systems. GLEAMS builds upon the foundations in CREAMS by adding components to simulate movement of water and chemicals within the crop root zone. Like CREAMS, GLEAMS is a continuous, daily simulation model.

GLEAMS predicts runoff using the SCS curve number method. Erosion is predicted based upon modifications to the Universal Soil Loss Equation. Surface runoff and eroded sediment, with chemicals in both the dissolved and sorbed phases, can be routed overland, in channels, and through impoundments.

GLEAMS divides the crop root zone into seven layers. The vadose zone between the root zone and the water table is not considered. The first layer has a thickness of 1 cm. This layer is assumed to be the portion of the soil that determines the mass of pesticide available for extraction into surface runoff. The thickness of the second layer is 1/6 of the root zone depth minus 1 cm for the first layer. The remaining 5 layers are each 1/6 of the root zone in thickness. This layering structure is fixed by the program. A strong correlation has been observed between pesticide concentrations in runoff and the concentration of pesticides in the top 1 cm of the soil profile (Leonard, 1988). Thus the authors of CREAMS and GLEAMS believe that a 1 cm active zone at the soil surface is required to maintain sensitivity of runoff concentrations to soil concentrations (Leonard and Knisel, 1987). Soil profile properties can vary with depth. The model weights the input values to establish average properties for each layer in the model. Percolation through the profile is based on the water-holding capacity of the soil as

in PRZM. Water in excess of field capacity drains to the next lower layer.

Pesticide transport within the root zone is by advection. No dispersive flux components are included. Volatilization is not considered. Pesticide applications can be partitioned between plant foliage and the soil surface. Different degradation rates can be specified for chemicals on the foliage and within the soil. Soil-applied chemicals can be incorporated to a specified depth.

The model will simulate up to ten chemicals simultaneously. This feature makes possible the observation of the effect of changes in chemical properties, e.g. partition coefficient, on resulting leaching losses with one model run. The model can also simulate the formation, fate, and transport of degradation products of the parent chemicals.

3.3.3 Coupled saturated/unsaturated zone transport models

The root/vadose zone models described above are important tools for assessing the mobility of pesticides within the unsaturated zone. The concern expressed by the public and governmental officials relate to pesticide residues in groundwater supplies used for drinking water. Thus the unsaturated zone models need to be linked to saturated zone transport models so that the concentrations and transport of pesticides within aquifers can be calculated.

As described above, MOUSE (Steenhuis et al., 1987) can predict the transport of pesticides in a vertical, two-dimensional cross section of a water table aquifer. Jones et al. (1987) coupled the PRZM model to a two-dimensional saturated zone transport model to predict the movement of

aldicarb residues within a shallow water table aquifer. Dean and Carsel (1988) reported on progress in linking PRZM to a two-dimensional saturated transport model. The linked model will use PRZM for simulating the root zone, a one-dimensional transport model for the vadose zone, and a two-dimensional saturated zone model which can simulate confined, unconfined, and leaky confined aquifers. The saturated zone model will also simulate pumping from the aquifer(s). The linked model is expected to be released for testing during the fall of 1988.

3.3.4 Model testing and uncertainty

Methods (such as described above) to predict the transport of the chemicals used by agriculture are needed by regulators in order to assess the impacts on surface water and groundwater quality from the use of these chemicals. Field testing of the contamination potential of all chemicals registered for use by agriculture would be infeasible due to both cost and time constraints. Since decisions regarding chemical use will be made based upon the results of transport models, it is important to understand the errors and uncertainty associated with the models. Each model or method will have errors associated with the assumptions relating to the description of the system, choice of equations to represent the system, and input parameters required by the models. There are some general points that can be made regarding the uncertainties inherent in deterministic, physically based models such as PRZM and GLEAMS which were described previously. An excellent discussion of the uncertainty in transport models is presented by Leonard and Knisel (1988).

Limitations of the conceptual formulation of the system that is described by a model lead to uncertainty in the results. Most deterministic models assume that some of the physical properties of the system are uniform with respect to location. That is, soil properties such as porosity, water-holding capacity, and organic matter content are constant across the field, although most models will allow these types of properties to vary with depth in the soil profile. Furthermore, variations in pore sizes within the soil, which can cause uneven water velocity distributions, are usually not considered. Each model will represent a system (ie. the crop root zone) in varying levels of detail.

The equations which are used to represent the fate and transport processes have limitations and uncertainties. For example, PRZM and GLEAMS both use the SCS curve number method for partitioning rainfall between runoff and infiltration. This method utilizes daily rainfall records and does not consider the effects of rainfall intensity on the runoff process. Testing of the CREAMS model (Knisel, 1980), from which GLEAMS was derived, showed that the daily hydrology option represented average annual runoff volumes well, but did not do as well with daily and monthly runoff volumes (Smith and Williams, 1980). PRZM and GLEAMS both utilize modified versions of the USLE (Wischmeier and Smith, 1978) for prediction of daily soil erosion. The USLE was developed for long-term (20-yr) average annual erosion rates. Although these modifications have been tested, the basis of these methods is the USLE which is an empirical equation derived for long-term average predictions. Many transport models utilize the linear form of the Freundlich equation (Equation 3.1) to describe the partitioning of a chemical between the dissolved and

adsorbed phases. Rao and Davidson (1980) indicate that the assumption of linearity can lead to errors on the order of a factor of two to three. The previous examples illustrate that the mathematical representations of processes used in models often have inherent inaccuracies and uncertainties.

The parameters which are required by the models to solve the equations which describe the system also have inherent uncertainties associated with them. Jury, (1985), in a review of the literature, reported coefficients of variation (CV) from field measurements of several soil physical properties. Soil porosity was found to have a mean CV of 10%. Bulk density measurement had a CV of 9%. Determinations of particle size fractions had an average CV of 28%, with a range of 3 to 55%. The water-holding capacity of the soil at matric potentials of 0.1 and 15 bars had a CV of 15 and 25%, respectively. Measurements of saturated hydraulic conductivity and infiltration rates showed a CV of 124 and 72%, respectively. In a study by Jury et al. (1986), the partition coefficient, K_d, of napropamide measured on 36 samples from a 1.44-ha field had a CV of 31%. Rao and Davidson (1980) reported that the normalized partition coefficient, K_{oc}, reported from individual studies generally had a CV of 40-60%. The variability of the properties reported above are not necessarily due to the fact the samples were taken over large areas. Jury (1985) reported that one author had reported that up to 50% of the variation in a parameter over a field occurred within a 1 m^2 area.

Given the uncertainties associated with models and the parameters required by the models as outlined briefly above, how closely must a

model match field observations in order to be considered validated (determined to accurately represent the system)? Leonard and Knisel (1988) indicate that there are no standard criteria for model validation. Since the spatial distribution of variations in soil properties is usually unknown, it would be unreasonable to expect any model to exactly match point measurements from a field study. Hedden (1986) reported that participants of the Predictive Exposure Assessment Workshop sponsored by the U. S. EPA in Atlanta, GA, on April 27-29, 1982, agreed on two criteria for model acceptance. For screening applications of the model (limited site-specific data and not calibrated to previous data from the site), the model should be able to replicate measured field data within an order of magnitude. For site-specific applications (parameters measured on-site and with the model calibrated to the site), the model should be able to match the field observations within a factor of two. The screening level criteria seems to be quite reasonable when all of the sources of error and uncertainty are considered. The site-specific criteria, however, may be difficult to meet by even the best models using carefully measured site-specific parameters.

The fact that models can not be expected to exactly replicate field measured values does not mean that they have no value. Models that have been verified (ie. their response to changes in parameters reflect what would be expected based on knowledge of the system) can be used with some confidence to evaluate the differences in predicted leaching of different chemicals or, perhaps, differences in leaching of a single chemical due to different climatic or management conditions.

3.4 Field Studies of Pesticide Transport

Field-scale studies of pesticide runoff and leaching have, until recently, been very limited. Studies of sufficient detail to be used for the validation and testing of transport models have been limited due to three factors, according to Donigian and Rao (1986b):

1. Most field studies have focused on either chemical leaching or surface runoff from watersheds; few studies have examined both.
2. Since sampling and analysis costs associated with pesticide leaching are high, most studies are of short duration.
3. Most studies were designed for purposes other than developing data sets for model testing and therefore are incomplete with regard to measurement of all the required model input parameters.

In this section, four field studies are reviewed. Methods of sampling and monitoring will be emphasized. Some of the studies were conducted specifically for model validation and testing purposes. A review of the Big Spring Basin study is included due to the unique conditions in the study area.

3.4.1 Aldicarb in Florida citrus groves

A three-year field study of the movement and degradation of aldicarb in both the unsaturated zone and a shallow water table was conducted at two locations in Florida (Hornsby et al., 1983; Jones et al., 1987). The two locations are referred to as the Oviedo site and the Lake Hamilton site. At both locations, aldicarb was applied to bedded citrus trees located on coarse-textured soils. Some of the soils at the Oviedo site had a thick organic layer overlying the coarse textured

subsoil. The Oviedo site is in the flatwoods area and is poorly drained. The Lake Hamilton site was located on a sand ridge. Drainage of the upper soil layers was very rapid. The Oviedo site encompassed 3.6 ha of treated area and the other site encompassed approximately 1.7 ha.

Aldicarb was banded along each side of the trees and incorporated to a depth of 5 cm. At the Oviedo site, soil samples were collected in 30 cm increments to a depth of 150 cm. At the Lake Hamilton site, soil samples were collected in 30 cm increments to a depth of 60 cm, and then in 60 cm increments to a depth of 300 cm. Soil samples were collected using a bucket auger and were transferred into plastic bags for storage at -20°C until analyzed. The soil samples were collected monthly for six months following the first application of aldicarb in 1983. Undisturbed soil cores and bulk soil samples were also collected from untreated areas at each site for laboratory determination of soil and chemical properties.

At each site, two clusters of observation wells were installed within the treated area, and additional well clusters were located upgradient and downgradient of the treated area. The wells were screened at depths of 2, 3, 5, and 6 m at the Oviedo site, and at depths ranging from 5 to 15 m, depending on location, at the Lake Hamilton site. Water samples were usually collected with a peristaltic pump. At least 5 well volumes were pumped prior to collecting a sample for analysis. When flowrates into the well were too slow to permit pumping of 5 well volumes, the wells were evacuated and the water entering the wells was pumped for an additional 5 minutes prior to collection of the sample. The groundwater temperature, pH, and conductivity were measured during

sampling. Water samples were collected monthly throughout the study. The storage conditions prior to analysis were not specified.

Results from the first 6 months of the study were reported by Hornsby et al. (1983). Results are reported in terms of total toxic residues (TTR), which is the sum of residues of aldicarb, aldicarb sulfoxide, and aldicarb sulfone. Fifteen days after application, TTR were not detected below 30 cm at the Oviedo site, but were detected in all replicates at the Lake Hamilton site to a depth of 120 cm. After 120 days, TTR were detected at the deepest sampling depths (150 cm at Oviedo, and 300 cm at Lake Hamilton) at both sites. No TTR were observed at the Oviedo site in any of the observation wells during the first six months. Two wells within the treated area at the Lake Hamilton site showed measurable levels of TTR. In one well, TTR levels as high as 1.2 mg/L were measured approximately 130 days after application. Data relating to rainfall or irrigation during the study were not presented.

Jones et al. (1983) used the data from the aldicarb study above to evaluate three pesticide transport models. One of the models tested was PRZM (Carsel et al., 1984). Agreement between PRZM predicted movement of aldicarb and the observed data was good. A sensitivity analysis was performed to demonstrate the response of PRZM to variations in several soil and pesticide properties. Jones et al. (1987) presented results from the Lake Hamilton site in which water samples from the shallow water table were collected from a network of 174 wells over a period of three years. These data were used to evaluate predictions from a linkage of the PRZM model to a one- or two-dimensional saturated transport model. The linked model was developed to allow predictions of the extent of

lateral transport of TTR which have entered a shallow water table. PRZM was used to predict daily mass loadings of aldicarb to the top of the water table. Results of the saturated zone modeling were in reasonably good agreement with the observed concentrations in the wells and the rate of lateral movement.

3.4.2 Comparison of tillage effects in Maryland

Paired watersheds were established in 1984 on the Eastern Shore of Maryland to observe the impacts of tillage practices on agricultural chemical leaching and runoff. The experimental design and early results have been reported by Brinsfield et al. (1987, 1988). One of the objectives of the experiments was to generate a data set for testing and validation of pesticide transport models. One watershed was used to grow corn using conventional tillage (CT) practices, and on the other watershed corn was grown using no-till (NT) methods. The CT watershed is approximately 6 ha in size, and the NT watershed covers approximately 8.9 ha. The soils in both watersheds are silty, well-drained, and nearly level.

Soil samples were collected at 5 locations in each watershed 4 times per year. The samples were collected using a hand auger in 15 cm increments to a depth of 120 m.

Monitoring wells made of 6.35 cm diameter PVC were installed to depths of 3-4 m on 30 m centers in each field. The wells were arranged to divide each field into four quadrants. The wells were installed so that only the top of the water table would be sampled. A bentonite-soil mixture was used to seal the top 0.5 m of each well. Well samples were

collected monthly. The wells were pumped for 5 minutes prior to collecting a sample for analysis.

To monitor surface runoff, H-flumes with automatic samplers and recorders were installed in the outlets of the watersheds. All samples were frozen for transport and storage prior to analysis. Details of the analytical procedures used for pesticide residue analysis are presented by Brinsfield et al. (1987).

Gravity-fed lysimeters were installed horizontally through the walls of a reinforced pit to collect samples of percolating water. The lysimeters were installed at a depth of 1 m below the soil surface. Three lysimeters were installed in each pit. These lysimeters collect samples of saturated flow percolating through the root zone. Samples were collected from these lysimeters after each rainfall event.

Herbicide treatments were the same for both watersheds. Atrazine, metolachlor, and simazine were applied pre-emergence at the rate of 1.68 kg AI (active ingredient)/ha. Cyanazine was applied at 2.24 kg AI/ha, and carbofuran at 1.12 kg AI/ha, both pre-emergence. Dicamba was applied post-emergence at a rate of 0.55 kg AI/ha.

Leachate collected in the lysimeters during January, 1985, had atrazine concentrations as high as 2 μg/L. After planting in 1985, no leachate samples were collected in the CT watershed until September. Atrazine and metolachlor concentrations in those samples ranged from 1-2 μg/L. Simazine was detected in only one sample, and cyanazine was not detected. In the NT watershed, samples collected in July had concentrations of atrazine at 8-10 μg/L, simazine at 7-10 μg/L, cyanazine at less than 1 μg/L, and metolachlor at less than 2 μg/L. Leachate from

the NT watershed in the fall of 1985 had similar concentrations to those collected from the CT watershed.

Groundwater samples collected 15 days after application in 1984 showed levels of atrazine, simazine, and cyanazine exceeding 1 μg/L. The concentration of atrazine in one well reached 7 μg/L on this date. During late summer and fall, atrazine was the only pesticide detected in the wells. Pesticide concentrations in the groundwater were similar for the two watersheds, although the concentrations were somewhat higher during the growing season in the NT watershed. In April, 1986, (prior to application) atrazine concentrations of 4 μg/L were observed in the water table on both watersheds. This indicates that atrazine may be persistent in the lower soil zones and in the water table.

3.4.3 Aldicarb movement in the Dougherty Plain of Georgia

The U. S. Environmental Protection Agency and the U. S. Geological Survey began a study in 1982 to observe the movement of aldicarb and its residues in the unsaturated and saturated zones at a field site in Lee County, in southwestern Georgia. Aldicarb is used as an insecticide and nematicide on peanuts grown on the site. One of the primary objectives was to develop an extensive database of soil, land use, geologic, and pesticide data for use in the validation and testing of the PRZM (Carsel et al., 1984) model. Different aspects of this study have been reported by a number of investigators (e.g. Cooper, 1986; Rao et al., 1986; Hook, 1987; Hedden, 1986; Smith and Carsel, 1986).

The study site covers an area of approximately 4.5 ha. Four soils are mapped in the field. All have a fine-loamy texture. Below a depth

of approximately 1 m there are layers of clay separating zones of coarser sand and gravel. The conductivity of the clay layers is very low, which suggests that perched water tables may form on these layers and cause lateral transport of leached pesticides. There is a shallow water table at the site which can vary in position by as much a 6 m during a year.

Soil samples were collected from the site to characterize soil properties and pesticide sorption and decay characteristics. Geologic information was collected from holes bored to the top of the Ocala Limestone. The residuum was approximately 13 m thick. The Ocala Limestone is a part of the Floridan aquifer system. Four wells were cased into the Floridan aquifer for measurement of water levels. A weather station was installed at the site to collect meteorological data.

Statistical procedures were used to determine that 20 monitoring sites would accurately reflect the fate and transport of aldicarb at this site. The locations of the monitoring sites were randomly selected and distributed between the three major soil series based upon the relative area in each series.

Each monitoring site was equipped with an impressive array of instruments for monitoring of conditions and collecting samples. Five tensiometers were installed to a depth of 150 cm for monitoring soil water content. The tensiometers were monitored and serviced three times per week. Five thermistors were installed to a depth of 115 cm for measurement of soil temperatures. The thermistors were monitored three times per week during the middle of the afternoon in order to estimate maximum soil temperatures. Three soil solution samplers were installed

at depths of 1.5, 2.1, and 2.7 m. The samplers were made using stainless steel for the body, a high-flow ceramic cup, and teflon tubing for sample collection and applying the vacuum. A silica flour slurry was poured around each sampler to insure good contact with the surrounding soil. The vacuum and sample lines were buried to avoid interference during field operations. Vacuum was applied to the samplers for a period of 24 hours prior to collection of the sample.

At 15 of the monitoring sites, permanent stainless steel monitoring wells were drilled to a depth of approximately 4.6 m. A stainless steel screen 0.6 m in length was placed at the bottom of each well. A gravel pack was placed around the screen and a cement grout was placed from the gravel to the top of the finished well. The wells were finished so that the top of the well was approximately 0.6 m below the soil surface so as not to interfere with cropping operations. After field operations are complete, the wells are extended above the soil surface. Water samples are collected using a dedicated teflon tube (one per well) and a peristaltic pump. The 250 mL glass sample containers were connected in line between the well and the pump to prevent cross contamination. The wells were typically pumped for 5-7 minutes prior to collecting a sample.

Soil samples were collected using a hand auger in 15 cm increments to a depth of 120 cm. After each sample was collected, gravel and plant material was removed and then the sample was sealed in a metal container.

The references which were obtained for this review did not report any results of pesticide monitoring from the field site. The detailed monitoring network and experimental design used at this site should produce a valuable data set for model validation and testing.

3.4.4 Big Spring Basin in Iowa.

The Big Spring Basin is a 267 km^2 groundwater basin located in northeastern Iowa. The basin is entirely agricultural with approximately 60% of the land area in row crops. The basin has been extensively monitored and characterized, and results from these studies have been presented by a number of investigators (Libra et al., 1986; Kelley et al., 1986; Hallberg, 1986; Libra et al., 1987). Over 85% of the basin's groundwater is discharged through Big Spring. Thus, investigators have an easily accessible point for monitoring average groundwater quality in the basin as affected by agricultural activities. Big Spring is a karst spring with an estimated 10% of flow contributed by directed recharge through sinkholes. By using hydrograph separation techniques, the investigators can determine the water quality effects of both normal infiltration and direct recharge through the sinkholes.

Four years of monitoring have shown flow-weighted mean concentrations of NO_3-N ranging from 7-11 mg/L. Combined losses of NO_3-N in both surface water and groundwater amount to 33-55% of the average annual fertilizer nitrogen applied in the basin. Historic records indicate that the magnitude of NO_3-N concentrations have increased by 200-300% over the last 20 years. This corresponds to a 200-300% increase in the application of nitrogen fertilizers during this period.

The herbicide atrazine is the only pesticide that is always present in the discharge from Big Spring. Flow-weighted mean concentrations of atrazine are less than 1 $\mu g/L$, but the average concentrations have steadily increased during four years of monitoring. Total losses of

atrazine in the groundwater amount to less than 0.1% of the annual application. Pesticide concentrations in surface waters are generally an order of magnitude higher than observed in the discharge from Big Spring. Peak concentrations of pesticides occur following recharge events in the spring after crops have been planted.

3.5 Summary

There is a growing body of evidence that pesticide residues are being leached to groundwater in some areas of the country. The U. S. EPA recognizes that at least 19 pesticides have been found in groundwater in 24 states as a result of agricultural practices (U. S. EPA, 1987a). Many of the pesticide detections in groundwater have been from the use of nematicides, which in general need to be very soluble in order to be effective. The other major class of compounds found in groundwater from agricultural practices is herbicides. The herbicides atrazine and alachlor are used over large areas in many regions of the country, and have been frequently detected in groundwater. Nitrates from agriculturally applied fertilizers have also been found in groundwater. The health risks associated with the low concentrations (typically less than 10 $\mu g/L$) of pesticides in drinking water are still unknown. There are documented health risks, however, to infants drinking water with high levels of nitrates. The agricultural production systems in this country will continue to require large inputs of chemical fertilizers and pesticides. Scientists and governmental regulators must identify ways to protect groundwater supplies from contamination while allowing farmers to use the chemical inputs required to maintain yields. Simulation models

will play an important role in evaluating the contamination potential from applications of pesticides and fertilizers and assess the benefits of modifications to current agricultural management practices (application methods, timing, chemical formulations, tillage practices, etc.).

There are many factors which influence the mobility and persistence of pesticides in the environment. Soil physical properties, chemical properties, crop characteristics, environmental factors, and the interactions among them determine the fate of agriculturally applied chemicals. Many of the processes involved in the transport and degradation of pesticides in the environment are poorly understood, and the mathematical equations used to represent these processes are simplifications based on experimental observations. The soil properties and environmental factors which strongly influence the fate of a chemical can vary significantly within small areas.

Methods to predict the fate of agriculturally applied chemicals range from simple indices to complex mathematical research models. Models which can represent the effects of agricultural management practices on the transport of chemicals are being used by governmental regulators as part of the chemical registration process. Most of the management models developed to date are designed to represent the processes on the soil and plant surfaces, within the crop root zone and possibly the unsaturated zone between the root zone and the water table. New model developments will incorporate groundwater transport models to assess how far and at what rate a chemical that leaches into groundwater will move. There are many sources of uncertainty and error associated

with model predictions. Thus models should not be expected to provide exact predictions of transport and fate within a field. There have been a limited number of studies however, which provide data of sufficient detail to assess how well the models do represent average transport within a field. In order to gain confidence in the use of models for pesticide fate and transport predictions, many new studies in various regions throughout the country are needed. To be of real value in model testing and validation, these studies should last for several years. For models which require calibration, a year or more of data may be needed to calibrate the models and then several additional years of data from that site will be needed to test the predictions of the calibrated models.

CHAPTER 4
EXPERIMENTAL METHODS

4.1 Field Site Description

The study site is located near Tifton, Georgia, in the coastal plain physiographic region of the southeastern U.S. The geology of this area has been described by Asmussen et al. (1986). The site is part of a farm rented by the University of Georgia Coastal Plain Experiment Station which is referred to as Gopher Ridge in honor of the many gopher tortoises which make their home on the edges of the fields and in the woods nearby.

The study site covers 0.7 ha in the northwest corner of a 2.3-ha field. The field was developed for irrigated agricultural research. Irrigation sprinkler risers are located on a 12 by 12 m grid. Supply lines for irrigation water are buried approximately 1 m below the soil surface. The field was removed from active crop research in 1982. At that time the field was deep tilled in both north-south and east-west directions to remove possible residual tillage effects. A permanent bahia grass cover was established and fertilized and irrigated as needed. No pesticides were applied after the grass cover was established. The field was maintained in this condition until the spring of 1986 when instrumentation for this research was installed. The site is bounded on the north and west by trees. Just beyond the tree line on the western edge of the field, the surface elevation drops rapidly into a seepage

area where subsurface flows reemerge as surface water that flows to the Little River.

The soil on the study site is classified as a Lakeland sand (Typic Quartzipsamments, thermic, coated). The soil profile depth on this site ranges from 1.9 to 4.4 meters. Underlying the soil is a restricting layer consisting of tight clays. This restricting layer is the top of the Hawthorne formation which forms the confining layer over much of the aquifer system (Floridan) of southern Georgia and Florida. The presence of this restricting layer causes percolating rainfall or irrigation to saturate the soil above the layer and form a transient water table.

Previous work by Asmussen et al. (1986) had shown, through the use of ground penetrating radar (GPR), that the restricting layer below the study site would cause saturated flow above it to converge into channels. The presence of these channels made the site look promising for saturated zone monitoring because samples from wells located in these channels would be very likely to show the presence of any chemicals which were moving with the saturated flow. The maps drawn from the (GPR) descriptions also indicated that the slope of the restricting layer near the study area boundaries was generally away from the study area. This would minimize influences of saturated flows coming into the site from other areas.

Figure 4.1 shows the elevations of both the soil surface and restricting layer for the 0.7-ha study site. The elevations given are relative to a local bench mark which was assigned an elevation of 30.48 m. The soil surface has a relatively uniform slope of approximately 4% towards the west. The restricting layer shows a more complicated

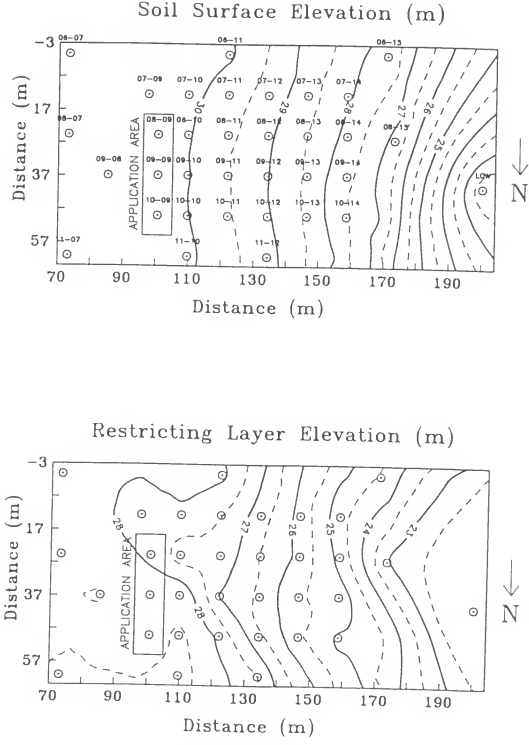


Figure 4.1. Contour maps of soil surface and restricting layer showing locations and ID labels of monitoring wells.

topography. Slopes of the restricting layer range from 1 to 15 percent, with the general direction of the slope also being towards the west. The fact that the soil is a coarse sand also was considered to be advantageous for monitoring pesticide movement. The high hydraulic conductivities and low clay and organic matter contents should result in increased leaching and movement of applied chemicals as compared with tighter soils. Another advantage of this site was the availability of irrigation which could be used to supplement the natural rainfall if required to maintain a dynamic flow regime.

This study was not intended to represent typical agricultural chemical usage and practices in the coastal plain of Georgia. The primary objective was to observe chemical movement within the unsaturated soil and in a shallow water table aquifer (shallow groundwater). The properties of the soil and restricting layer described above were suited for this objective.

4.2 Site Instrumentation

The movement of the applied chemicals was monitored using a combination of soil samples, soil-water (soil solution) samples from the unsaturated zone, and saturated zone samples. These samples were collected using augers, soil solution samplers, and monitoring wells, respectively. Soil sample collection required no permanent instrumentation, and the collection procedure will be described in a later section.

Samples of the water from unsaturated soil were collected using soil solution samplers. An excellent review of soil solution samplers is

presented by Litaor (1988). Smith and Carsel (1988) presented a design for a stainless steel solution sampler that do not react with pesticides during sampling. Samplers constructed of stainless steel were not economically feasible in this research.

The samplers used in this study were constructed of 4.2 cm OD, schedule 40 PVC and a 1 bar, high flow ceramic cup, 3.99 cm diameter by 19.05 cm long attached to the PVC pipe with epoxy. A 0.64 cm polypropylene tube was extended from the inside bottom of the ceramic cup to a bulkhead fitting on the top of the sampler. A second fitting was placed on the side of sampler, near the top, for attaching a vacuum line. The samplers were constructed in two lengths, 1.08 and 2.09 m. The polypropylene tubing used in the samplers was not tested for adsorption of atrazine and alachlor. This was not done since the solution samplers were to be used for collection of samples to be analyzed for inorganic chemicals such as bromide and nitrate. The volumes of samples collected from the solution samples were in general too small (less than 50 mL) to permit reliable quantification of pesticide residues.

The samplers were placed such that the center of the ceramic cup was located at depths of 61, 122, and 183 cm. The samplers were installed by augering a 5 cm hole to a depth that was approximately 10 cm less than the desired sampling depth. A piece of thin wall aluminum tubing with ID slightly smaller than the ceramic cup was then driven 20 cm beyond the augered hole, removing a core of soil. The sampler was pushed into the hole until seated on the bottom. A slurry of water and soil taken from a borrow pit adjacent to the site was then poured into the annulus between the PVC and soil. The top 12 cm of the hole was

widened to approximately 10 cm in diameter and was filled with a bentonite slurry to form a seal around the sampler and prevent direct flow from the surface down the side of the PVC pipe to the ceramic cup.

Figure 4.1 shows the location of the application area, which is the strip to which the herbicides and bromide tracer were applied. The samplers and three monitoring wells (08-09, 09-09, and 10-09) are within this area. The samplers were installed in groups of three at a distance of 3.05 m on either side of each well along a north-south axis. The samplers were assigned identification labels that indicated their position with respect to the wells and the depth to which they were installed, eg. the group of samplers located 3.05 m south of well 09-09 were assigned labels of 09S-2, 09S-4, and 09S-6 for depths of 61, 122, and 183 cm (2, 4, and 6 ft), respectively. A cross-section of the application area showing the locations of solution samplers and monitoring wells is shown in Figure 4.2.

A small instrument trailer was located approximately 4 m east of the application area. A vacuum pump located in the trailer was used to apply a vacuum to all samplers simultaneously through a manifold. The pump was capable of creating a vacuum of approximately 28 cm of Hg. A 0.64 cm diameter polypropylene sample tube was connected to the sample fitting on each sampler and routed back to the trailer where it was connected to a 50 mL polycarbonate sample container. All sample tubing was enclosed in a protective PVC conduit which was located 1.5 m from the samplers to avoid interference with chemical application in the vicinity of the samplers. Between the samplers and the PVC conduit, the stiff polypropylene vacuum and sample lines were fastened together and held

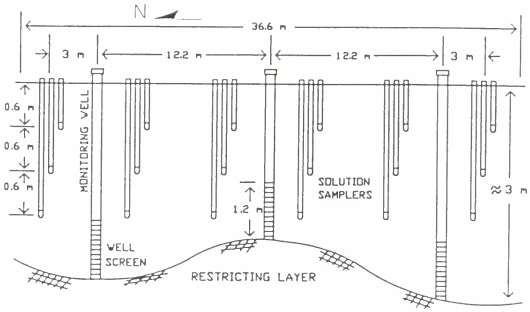


Figure 4.2. Cross-section of soil profile through application area showing locations of monitoring wells and soil solution samplers.

about 0.6 m above the soil surface to minimize interference around the samplers. When it was time to collect the samples from the samplers, the vacuum was switched to the sample collection side and the vacuum side was opened to atmospheric pressure. Any water that had accumulated in the samplers would then be pulled into the sample containers.

Monitoring wells for collection of samples from the saturated zone and measurement of the water table elevation were installed during May of 1986. The wells were constructed of 6.3 cm diameter, schedule 40 PVC and were slotted using a veneer blade on a radial arm saw. Three rows of slots were cut along the circumference of the well. Each slot was approximately one-sixth as long as the pipe circumference. The slots were spaced approximately 2.5 cm apart over the bottom 1.22 m of the well. Although several manufacturers offer slotted PVC well screens,

these were beyond the budgetary constraints of this project. Some existing wells, installed by the USDA-ARS Southeast Watershed Research Laboratory in conjunction with the GPR mapping by Asmussen et al. (1986) were also used. Conversations with the technicians involved with the installation revealed that the wells were constructed of the same materials as described above but were perforated with tiny drill holes instead of being slotted. They were unable to recall the diameter of the holes or the extent of the perforation above the bottom of the well. Appendix A lists statistics associated with each well and indicates which wells were installed by USDA.

The wells were installed by hand augering a 10 cm diameter hole down to the top of the restricting layer. The restricting layer was identified by a sudden change from yellowish-white sand to red clay mixed with small rocks. The change was very abrupt and the effort required to auger through the clay was significantly greater than to auger through the coarse sand. A PVC end cap was slipped onto the end of the well and held in place by friction during installation of the well. Fine gravel was placed around the wells in the zone of the slots in an attempt to minimize sand migration into the wells through the relatively coarse slots. Soil from a nearby borrow pit was used to fill the hole around the well to within 12 cm of the surface. Ten centimeters of a water and bentonite slurry was then added to form a seal around the well. The final 2 cm was filled with soil. The USDA augered down to the restricting layer with a hollow stem auger on a small drill rig. The well was slipped into the center of the auger and the auger was

withdrawn. No details on backfill procedures used by the USDA are available.

The wells were continuous from the restricting layer to a height of approximately 50 cm above the soil surface. No solvent weld joints or connections were used. Each well was fitted with a 0.64 cm diameter polypropylene tube which extended from approximately 2.5 cm above the bottom of the well through a #2 rubber stopper placed in a vented PVC cap. The polypropylene tubes were not tested for adsorption of atrazine and alachlor. The caps were vented by milling small channels into opposite sides of the inside of the cap. This was done to prevent a vacuum from forming in the well during sampling.

The wells were installed on a 12 by 12 m grid corresponding to the locations of existing sprinkler risers. The wells were offset by approximately 50 cm to the west of the sprinkler risers to avoid hitting supply lines beneath the soil surface. In the application area the wells and solution samplers were offset from the sprinkler risers by about 3.05 m so that the risers and supply lines would not interfere with the downward movement of chemicals within the vicinity of the wells and samplers. The monitoring wells were assigned ID labels to indicate their position relative to the sprinkler riser in the SE corner of the 2.7 ha field on which the experimental site is located. Figure 4.1 shows the locations of the wells and the associated ID labels. Well 08-15 is located at the edge of the tree line bordering this side of the study site. One well is located in the woods approximately 30 m west northwest of well 08-15. This area is a seepage zone where subsurface flows

reemerge as surface water and flow to the Little River. This well is referred to as "LOW".

Additional instrumentation installed at the site consists of a weighing rain gage which was located near well 09-12, a water table recorder which was located near well 08-12, tensiometers for measuring the water content of the unsaturated soil, and a "deep" well located between wells 08-13 and 09-13.

The rain gage is a US Weather Bureau standard weighing bucket rain gage with a seven day chart and 30.5 cm capacity. The rain gage was calibrated using standard calibration weights after installation.

The water table recorder was installed to provide a continuous record of the water table elevation to supplement the weekly measurements taken on all wells. The recorder was equipped with a seven day clock and a drum type chart recorder.

Eight tensiometers were installed around each set of solution samplers. The tensiometers were water filled and connected with very small tubing to a mercury manometer board. The tensiometers were installed at depths of 30, 60, 90, 110, 122, 140, and 183 cm. There were two tensiometers located at the 60 cm depth. The tubing connecting the tensiometers to the manometer boards was routed above the soil surface with the vacuum and sample lines as noted above.

The "deep" well was installed by drilling a 10 cm diameter hole inside of a 11.4 cm diameter PVC casing. The casing was pushed down as the auger advanced. The casing was installed in this manner using 1.5 m sections to a depth of approximately 12.2 m below soil surface. The last 3 m of the well was located in a saturated formation that liquified

during drilling. The observation well was made of a 1.5 m section of 6.3 cm diameter commercial PVC well screening solvent-welded to two 6.1 m sections of schedule 40 PVC. This was jetted down inside of the casing until it bottomed out at the bottom of the previously augered hole. After placement of the well, a mixture of bentonite and water was poured into the area between the casing and well up to the top of the casing. The purpose of this well was to observe the piezometric head difference across the restricting layer.

4.3 Chemical Applications

The first application of chemicals to the experimental site occurred on 11/12/86. On the day preceding this first application, the entire field site was rotary mowed. The grass within the application area was cut to a height of approximately 5 cm. All dead grass and clippings were raked up and removed from the area prior to application. The application area consists of a strip 36.6 m long by 9.14 m wide as shown in Figure 4.1.

Atrazine and alachlor were applied simultaneously on November 12. Atrazine was applied in the form of AAtrex (Ciba-Geigy Corp.) which is an emulsifiable concentrate containing 0.479 kg AI (active ingredient)/L (4 lb/gal). Alachlor was applied in the form of Lasso (Monsanto Agricultural Products Co.) which is also an emulsifiable concentrate containing 0.479 kg AI/L. The herbicides were applied using a self-propelled boom sprayer with provisions for injecting chemicals directly into the water stream (Sumner et al., 1987). The boom length on the sprayer is 9.14 m.

The intended application rate of the herbicides was 4.5 kg AI/ha (4 lb/ac). One liter of herbicide solution was prepared by mixing 313 mL of each of the chemicals with 374 mL of deionized water. The sprayer was operated at a velocity of 3.05 m/min moving from south to north along the edge of the application area. The chemical solution was injected into the water stream of the sprayer using an injection pump calibrated to deliver 83 mL/min. The water pressure at the inlet of the sprayer was 207 kPa. The pressure at the spray nozzles was maintained at 138 kPa. Despite the calibration of the injection pump and measurement of sprayer ground speed, the chemical solution ran out as the sprayer reached well 10-09 which is 6.1 m short of the intended end of the application area. The application of the herbicides was considered complete at this point, and the remaining portion of the application area was left untreated.

Fourteen 0.35 l plastic cups were randomly placed within the application area. The cups were supported upright in holders at a height of approximately 35 cm above the soil surface. The cups were used to collect samples of the application solution for analysis of chemical concentrations, determination of the depth of water applied to the area during application, and uniformity of chemical and water application. The use of these cups and holders has been tested and found to accurately reflect water application amounts (Stansell et al., 1982).

Immediately after completing the application of the herbicides, the sprinkler irrigation system was started and 5.1 cm of water was applied over the entire study site. This irrigation was intended to wash the

herbicides off of the grass foliage and move them into the soil profile to minimize volatilization losses from the soil and plant surfaces.

Bromide in the form of potassium bromide (KBr) solution was applied to the application area using the same sprayer on 11/17/86. There was a light drizzle of rain during application. Five hundred grams of KBr was dissolved in 1050 mL of deionized water and injected into the sprayer as described above. This was equivalent to an application rate of 10 kg/ha of bromide. The sprayer again was operated at a nozzle pressure of 138 kPa, and a ground speed of 3.05 m/min. Fourteen collectors in the same locations as for the herbicide application were used to collect application samples.

No further chemical applications were made prior to fertilization of the grass on 4/16/87. The fertilizer was applied at a rate of 560 kg/ha of 5-10-15 using a tractor-mounted broadcast spreader. Fifteen percent of the nitrogen in the fertilizer was in the form of nitrate nitrogen (NO_3-N). This is equivalent to applying 18.6 kg/ha of nitrate (NO_3).

In an effort to further characterize bromide movement within the soil profile and determine flow velocities within the groundwater, an additional bromide application and a separate chloride application were made. On 4/27/87, KBr was applied to the application area using the sprayer utilized during the previous application. The application solution was made by dissolving 1.2 kg of KBr in 2.3 l of deionized water. The sprayer made two passes across the application area during which it applied approximately 1.6 l of the KBr solution. This was equivalent to an application rate of 17 kg/ha of bromide. Fifteen

plastic cups were used to catch application solution samples in the same manner as previously described. Immediately following application the field was irrigated. Irrigations continued daily for a week in order to raise the water table and provide plenty of infiltrating water to transport the bromide through the soil.

Prior to the beginning of irrigations on April 27, most of the wells on the site were dry. The water table began to rise on May 1 at which time 10 l of solution containing 500 g of potassium chloride (KCl) was poured directly into well 07-09 which is near the top of the site. It was anticipated that the high concentration of chloride in the solution could be followed downslope with the saturated flow and allow for determination of water table flow velocities.

4.4 Sample Collection and Storage

Samples were collected weekly (Monday) throughout the study. There were occasional periods of more frequent sampling (immediately after initial applications and during the last week of April through the middle of May).

The flint glass containers used for well sample collection and storage throughout this study did not have teflon lined caps. Therefore, a small piece of parafilm (a common laboratory film used for sealing beakers and containers to prevent evaporation and contamination) was stretched over the mouth of the bottle prior to screwing on the caps.

Samples of the application solutions of the herbicides and bromide were transferred to glass containers and placed in a cooler with ice

packs immediately after the sprayer had passed completely by the sample collector.

Soil samples were collected in one of two ways: taking 2.5 cm diameter by 5 cm long cores using a soil sampling probe, or using a 5 cm diameter stainless steel bucket auger. The soil sampling probe was generally used for collection of samples from the top 5 cm of the soil profile. When this method was used, 5 to 8 samples would be collected from a small area and composited into a plastic sample bag. This would represent one final sample for the soil surface at that location. For deeper samples the auger was used. The auger was used to remove soil to within approximately 5 cm of the desired sample depth. The auger was then cleaned to remove traces of soil, and a sample was collected which represented soil from a depth of 5 cm above to 5 cm below the target depth. The sample was carefully poured from the top of bucket into a plastic sample bag and sealed. The number of locations within the application area sampled depended on the number of depths to be sampled and ranged from 5 to 14. After collection, the soil samples were placed into coolers with ice packs for transport to Gainesville. Soil samples from outside of the application area were collected several times during the study to use as blanks and spikes during soil residue analysis.

Vacuum was applied to the solution samplers immediately upon arrival at the study site (7:00 - 8:00 am). The vacuum would typically be left on for 8 to 10 hours prior to collecting the soil solution samples. The vacuum applied to the samplers was approximately 28 cm of Hg. Near the end of the day the vacuum would be released and the samples would be drawn directly into individual containers. The containers are

made of polycarbonate with a capacity of 50 mL. The containers had polycarbonate screw caps for sealing. Immediately after all soil solution samples were collected, the sample containers were placed in a cooler for transport.

The elevation of the water table was measured using a well depth indicator with a stainless steel probe. The depth indicator would sound an audible alarm when the probe contacted water in the wells. The probe was attached to a flat cable with markings in feet and inches, with the smallest division being 1/4 in. Water depths were recorded early in the morning after arrival.

After the water table elevations in all wells were measured, the wells were pumped out to insure that the water to be sampled was representative of the surrounding water in the saturated zone at that time. When possible, the well was pumped dry. When the depth of water in the well exceeded approximately 0.4 to 0.5 m, the pumping rate was less than the rate of flow into the well. When this occurred, the well was pumped long enough to insure that 2-3 well volumes had been pulled from the well. A small, 12v battery powered, peristaltic pump was used to pump the wells and collect samples.

Samples were collected after all wells had been pumped as described above. A rubber stopper was attached to the intake side of the pump through a 1 m length of 1.25 cm OD Tygon tubing. The stopper also had a piece of Tygon tubing approximately 10 cm in length connected to it for attachment to the sampling tube in each well. The stopper was placed in a sample bottle and the short piece of tygon tubing was attached to the well sample tube. Since the pump was downstream from the sample con-

tainer, the only components common to each sample collection were the rubber stopper and the short piece of Tygon tubing. When a sample was collected, the initial water from the well was swirled around the bottle, and the bottle was then inverted to remove this rinse water. This served to rinse the Tygon tubing, stopper, and bottle. Thus, cross contamination between wells was minimized. The sample bottles used for the collection and storage of well samples had a capacity of 250 mL. Well samples were placed in coolers with ice packs for storage until they could be refrigerated.

All soil samples were frozen as soon as possible after collection and maintained at -18°C until preparation for analysis. All water samples were refrigerated after collection and maintained at 4°C until prepared for analysis.

4.5 Sample Analysis

4.5.1 Inorganic tracer analysis

The concentrations of the three inorganic chemicals of interest which were applied during this study were quantified using ion chromatography. A DIONEX QIC ion chromatograph (IC) was used for all analyses.

A DIONEX AS4A anion separation column was used with an AG4A guard column in place to remove organic contaminants prior to reaching the separation column. The IC was equipped with a conductivity detector connected to an external integrator/recorder. The IC was also equipped with an anion micromembrane suppressor to reduce the background

conductivity of the eluant and thus allow for greater sensitivity to the conductivity changes caused by the presence of anions in the sample.

There was no automatic sampling device with this instrument, so each sample was injected by hand. Approximately 1 mL of sample was loaded onto a sample loop prior to injection onto the column. The sample loop retained approximately 0.25 mL of the sample with the rest being discarded to a waste line. Between injections, the sample loop was flushed with 1 mL of deionized (DI) water. Prior to the guard column, the sample was passed through two filters rated at 30 and 5 microns, respectively, to remove solids from the sample. These filters were an integral part of the IC and the filter elements were changed whenever the system pressure was observed to be increasing above nominal levels.

The eluant used in these analyses was 2.2 millimolar (mM) sodium carbonate (0.933 g Na_2CO_3 in 4 l DI H_2O) and 0.75 mM sodium bicarbonate (0.25 g $NaHCO_3$ in the same 4 l of DI water). This solution was made fresh as needed. All references herein to deionized (DI) water refer to water that had been passed through carbon filters and ion exchange resins to produce DI water with a resistivity of at least 1 megohm. The regenerant solution was 0.025 N sulfuric acid (2.8 mL of concentrated H_2SO_4 in 4 l of DI water). The regenerant solution was passed through the micromembrane suppressor to reduce background conductivity.

In normal operation the eluant flowrate was approximately 2.0-2.5 mL/min, and regenerant flowrate was approximately 4 mL/min. The pressure at the discharge of the pump at the stated eluant flowrate was approximately 8,274 kPa (1200 psi).

A single injection could reveal the presence and concentrations (if standards were prepared) of the following anions (in order of increasing retention times): fluoride (F^-), chloride (Cl^-), bromide (Br^-), nitrate (NO_3^-), phosphate (PO_4^{3-}), and sulfate (SO_4^{2-}).

In ion chromatography, the retention times of the various anions are dependent upon total ionic strength of the sample, ionic strength of the individual ions, eluant flowrate, and temperature of the sample and eluant. Thus, the retention times could, and did, vary. When the integrator was set to calculate the areas under the peaks, it was found that the automatic selection of the beginning and ending points of peaks was not consistent. A small change in retention time could significantly alter the reported area for a given ion even when using duplicate injections. Better results were achieved by setting the integrator to report maximum peak height. This value was not sensitive to variations in the starting and stopping times of a peak as long the baseline was relatively stable.

Initial injections of water table samples from the experimental site revealed the presence Cl^- and SO_4^{2-} in all samples, and relatively high concentrations of NO_3^- in samples from well LOW. Standards were prepared using DI H_2O and oven-dried quantities of certified or primary standard grades of potassium chloride, potassium bromide, potassium nitrate, and potassium sulfate. The standards initially included Cl^- and SO_4^{2-} because of their presence in the samples. They were not used to quantify the concentrations of either species during initial sample analysis. When Cl^- was introduced into the water table as a tracer late in the experiment, sample concentrations of Cl^- were quantified. It was

observed that the response of the chromatogram to Cl^- was approximately twice the response to the other anions of interest. Thus, standards were prepared with Cl^- at half of the concentrations of the other species so that the responses of all species would be similar and on scale simultaneously. Standards were prepared with concentrations of the main species of interest ranging from 0.01 to 100.0 mg/L. A typical standard would contain 0.5 mg/L Cl^- and 1.0 mg/L of Br^-, NO_3^-, and SO_4^{2-}. It should be noted here that all references to nitrate (NO_3^-) indicate concentrations of NO_3^- and not NO_3-N (nitrate-nitrogen).

Samples were taken from the refrigerator and allowed to come to room temperature prior to injection. No sample preparation was performed. The analysis protocol typically followed the pattern of 3 standards, 10 samples, 3 standards, etc. The standards used were selected based upon the concentrations of the analytes being observed in the samples. Thus, standards were selected to bracket the observed values as closely as possible. Occasionally a sample would be reinjected to observe the repeatability of the analysis procedures. Samples from wells located away from the experimental site, including the deep well which supplies irrigation water to the farm, were regularly analyzed as field blanks (no Br^- would be expected; however, Cl^-, NO_3^-, and SO_4^{2-} could be present).

A piecewise linear fit to each sequence of injected standards was used to generate a function of the form: concentration = f(peak height). The piecewise fit was selected instead of linear regression because for some species (particularly high concentrations of Cl^-) a linear regression resulted in a negative y-axis intercept. This implies that

the species can generate a noticeable positive response and yet be calculated to have a negative concentration. It is expected that a positive intercept would be a normal result, i.e. there is some threshold concentration of the species required before the detector indicates a response. The piecewise fit insured that any positive response would result in a positive calculated concentration. Conversations with an organic chemist at the Pesticide Residue Laboratory of the USDA-ARS Southeast Watershed Research Laboratory indicated that the piecewise fit would be an acceptable method of generating a standard curve (Marti, 1987).

The standard curves generated on either end of the analysis of 10 samples were used to compute the concentrations of the species in the samples. The resulting concentrations were then linearly weighted based on sample position with respect to either set of standards, i.e. the first sample following the standards would be weighted towards the curve generated by the preceding standards and only slightly effected by the standard curve generated 9 samples later. The sample midway between standards would be evenly weighted between the two standard curves. In general, there was little drift in the instrument and the standard curves did not vary much over a period of hours.

4.5.2 Herbicide residue extraction

Analysis of samples for residues of atrazine and alachlor required different extraction procedures for soil and water samples. Once the extractions were completed, all samples were analyzed on a common gas chromatograph with identical operating conditions.

There are many published methods for preparing samples for determination of atrazine and alachlor residues (e.g., Rohde et al., 1981; Voznakova and Tatar, 1983). In general, the procedures are rather detailed and costly in terms of time and supplies. Dr. Willis Wheeler, Director of the Pesticide Residue Laboratory in the Food Science and Human Nutrition Department at the University of Florida, Gainesville, indicated that a simpler method of sample preparation might be developed which would be satisfactory in terms of the recovery of the pesticide of interest while being more economical in both the time required for sample preparation and expense (Wheeler, 1987). The more steps involved in the extraction and preparation of a sample, the more likely it is that something can go wrong and the residues lost. With these factors in mind, methods for extraction of the two herbicides from soil and water samples were developed which were in keeping with the budgetary constraints of the project and the time constraints on the analyst.

Extraction of the herbicide residues from water samples was done using a liquid-liquid extraction procedure. One hundred fifty milliliters of the sample water were placed in a quart mason jar along with 150 mL of pesticide-grade hexane. The jar was sealed with a standard mason jar lid which had been lined with a self-adhesive teflon film. The jar was agitated on a shaker table for thirty minutes after which the contents of the jar were poured into a labeled 500 mL separatory funnel. The sample water was drained through the separatory funnel back into the jar, leaving the hexane in the funnel. Another 150 mL of hexane was added to the jar and it was again agitated for 30 minutes. The contents of the jar were again added to the funnel. The

water was then drained and discarded. The hexane was filtered into a 500 mL boiling flask through sodium sulfate to remove any remaining water. Next, the boiling flask was placed on a rotary evaporator and the reduced in volume to near dryness. A few mL of fresh hexane was then added to the flask and swirled to wash the sides of the flask. This hexane was placed in a 10 mL volumetric flask. A few mL of hexane was again added to the boiling flask and the swirling repeated. After two rinses of the flask, the hexane in the volumetric flask was brought to a final volume of 10 mL. The finished sample was stored under refrigeration in test tubes with teflon lined screw closures. The initial sample volume of 150 mL and the final extracted volume of 10 mL indicate that this procedure concentrated the residues by a factor of 15. Blanks taken from remote wells as well as DI water were extracted as a check on the procedure. Spiked samples of well water and DI water were extracted to determine the recovery levels of the herbicides using the procedure described above.

Soil samples were removed from the freezer and allowed to air dry for one day prior to extraction. This was done to allow excess moisture to evaporate since the acetone used in the extraction process can absorb water which will not be removed by filtration through sodium sulfate as was done for the hexane extractions. Acetone was chosen as the solvent for soil extractions because it was observed that the water in the soil samples, or some other factor, tended to repel hexane. It did not appear that the hexane was adequately dispersing the soil particles.

A fifty gram portion of the air-dried soil sample was weighed and placed into the mason jar. One hundred mL of pesticide grade acetone

was then added to the soil sample. The sample was agitated for 30 minutes and the acetone was carefully decanted into a separate labeled glass container. Another 100 mL portion of acetone was added to the soil and the agitation was repeated for another 30 minutes. The acetone was poured into the container with the previous portion. Several rinses of acetone were poured through the extracted soil to remove any acetone left from the extractions. The acetone rinses were added to the acetone from the extractions and the entire volume was vacuum filtered through a 47 mm diameter filter with a 0.45 micron pore size. The filtrate was then reduced to near dryness on the rotary evaporator and brought to a final volume of 10 mL in acetone. Soil samples taken from outside the study area were extracted as field blanks and were spiked with known quantities of the herbicides and extracted as a check on the extraction and analysis procedures.

A subsample of approximately 10 g of each soil sample was taken to determine the soil-water content so that the concentrations of the herbicides in the soil could be reported on dry weight basis. Soil samples for soil-water content determinations were dried for 24 hours in an oven at 100°C.

4.5.3. Herbicide residue analysis

All herbicide residue samples were analyzed on a Hewlett Packard model 5840A gas chromatograph (GC). The GC was equipped with a 35 position autosampler and a model 5840 GC terminal (integrator). The GC had both electron capture (EC) and nitrogen-phosphorus (NP) detectors. During the early phases of the study (methods development), the electron

capture detector was used. This detector had a high sensitivity to alachlor and a lower sensitivity to atrazine. However, when field samples were analyzed, as opposed to DI water spiked with pesticides, it was observed that the EC detector was sensitive to many naturally-occurring compounds (the EC detector is sensitive to chlorine molecules) which had been extracted along with the pesticides. Thus, the output was so crowded with peaks that the quantities of atrazine and alachlor present could no longer be reliably determined. The NP detector is very sensitive to molecules of nitrogen and phosphorus and insensitive to almost anything else. When the samples were analyzed on this detector, the chromatograms were much cleaner and atrazine and alachlor were often the only visible peaks. The NP detector is somewhere between 5 and 10 times more sensitive to atrazine than it is to alachlor due to the greater number of nitrogen atoms in the structure of atrazine. The NP detector was operated with detector gas flowrates of air at 50 mL/min and hydrogen at 3 mL/min. The carrier gas was helium with a flowrate of 30 mL/min.

The column used in the GC was 1.83 m long with a 4 mm ID. The column was packed with 3% OV-17 (50% phenyl, methyl silicone) on 100/120 mesh Gas Chrom Q. The operating conditions were: injector port temperature set at 240°C, column temperature at 200°C, and detector temperature at 300°C.

The sample protocol used with the auto sampler was usually of the form: 4 standards, 1 solvent blank, 10 samples, 4 standards, 1 solvent blank, 10 samples, 4 standards, 1 solvent blank. The solvent blank was used to help prevent carryover from the last (and highest) standard into

the following sample. Carryover was normally not a problem, but the solvent blank would often show some trace of the herbicides.

Working standards of the two herbicides were prepared using reference standards provided by the EPA in Research Triangle Park, North Carolina. The initial standard was made by dissolving 10 mg of the reference into 10 mL of solvent yielding a concentration of 1 mg/mL (1000 mg/L). This standard was then used as the basis for subsequent working standards. The standards were prepared with the concentration of alachlor being 5 times greater than the concentration of atrazine so that the detector response to the chemicals would be nearly equal. Working standards of atrazine ranged from 0.01-500.0 mg/L with the concentrations of alachlor generally being 5 times higher as noted above (very high atrazine standards did not include alachlor). The 0.01 mg/L standard of atrazine represented the smallest concentration which was detectable without pushing the limits of machine and detector. The autosampler injected a volume of 4.8 μL. So an injection of 4.8 μL of 0.01 mg/L atrazine represented a lowest detectable mass of 10 nanograms of atrazine.

Whenever new standards were prepared, they were compared with the previous standards to assure similar response and that no mistakes had been made during the dilutions. Two sets of standards were made. One set was made in acetone for use in analyzing the soil sample extracts. The other set was made in hexane for use in analyzing the water sample extracts. Comparisons between the two sets of standards revealed no differences in response, but recommended procedures (Wheeler, 1987) dictate that the standards be made up in the same solvent as the samples.

The integrator available with the GC did not work properly. In order to quantify the amount of herbicides present in the samples, all peak heights were hand measured (a peak height mode, as used with the IC was not available on this integrator).

A linear regression was performed from the standards to give a relationship of the form: concentration = f(peak height). There were no problems with negative intercepts in these regressions as discussed in the section on ion chromatography. Sample concentrations were computed with the regression equations calculated from standards on either side of the samples. In order to account for drift in the detector response, the final concentrations were calculated by linearly weighting the concentrations computed from each set of standards as discussed previously. The NP detector had a tendency to drift and this correction for drift was usually needed.

CHAPTER 5
MODELING THE EXPERIMENTAL SITE

Two models were selected for the purpose of simulating the movement of the chemicals applied to the experimental site. The models selected for use were the Pesticide Root Zone Model, PRZM (Carsel et al., 1984), version 2, and Groundwater Loading Effects of Agricultural Management Systems, GLEAMS (Leonard et al., 1987), version 1.8.53. These models were selected because they were designed specifically to simulate pesticide transport through the root zone of a crop and reflect influences of agricultural management practices such as tillage. Reference to the manual for GLEAMS includes the documentation for the CREAMS model (Knisel, 1980) from which GLEAMS was derived as well as the supplementary GLEAMS user manual which is provided with the model code and describes the differences in input data sets between CREAMS and GLEAMS.

This chapter will discuss the selection of input values used in the models. Only the parameters relevant to the results will be discussed. There are parameters in both models for which values were selected, but which had no bearing on the results to be presented. For example the models utilize the Universal Soil Loss Equation, USLE, (Wischmeier and Smith, 1978) for prediction of soil erosion, however, in the simulations surface runoff was never predicted and therefore the parameters chosen for use with the USLE did not affect the reported results. There are

many parameters such as rainfall, pesticide properties, and soil characteristics which are common to both models. Thus, the selection of common parameter values will be discussed first, followed by selection of values for parameters which are unique to each model.

5.1 Selection of Common Input Parameter Values

5.1.1 Rainfall and irrigation

Both models use daily rainfall data. The formats of the rainfall files for the models are different and PRZM reads in values in centimeters while GLEAMS reads in values in hundredths of an inch.

The data used to create the precipitation files came from a combination of two rain gages. As stated previously, one weighing rain gage is centrally located within the experimental site. This rain gage was installed in June of 1986. A second rain gage is located approximately 300 m north-northeast of the experimental site. This gage is a tipping bucket type rain gage that is connected to a data logger. All rainfall data used in the simulations came from this off-site gage since the data from it was already on a computer and available. The rainfall amounts recorded in both gages agreed well. The gage located on the site was used to supplement the rainfall record with amounts of irrigation applied to the site. This rainfall plus irrigation file was then manipulated into the units and formats required by each model, and checked to insure that the two formats contained identical information.

5.1.2 Soil properties

Both models use the Soil Conservation Service (SCS) curve number method (USDA-SCS, 1972) to partition rainfall between runoff and infiltration. The runoff curve number was selected from Table 9 in the PRZM manual and was chosen based on the assumption that the bahia grass cover could be assumed to be similar to a pasture in good condition without contouring (Lakeland sand is classified as being in hydrologic soil group A).

Physical descriptions of the soil profile were obtained from two sources. Hook (1985) measured properties of the soil in another section of the farm on which the experimental site is located. The data collected by Hook (1985) were measured within the top 120 cm of the soil profile. The soils on the farm are uniformly classified as either a Lakeland sand or Bonifay sand. The primary differentiation between the soils is the depth to the restricting layer with the Lakeland soil being deeper than the Bonifay. Soil physical properties such as water retention and hydraulic conductivities are considered to be the same between these soils on this farm. The second source of data used to determine soil properties is a soil characterization report for Florida soils prepared by the Soil Science Department at the University of Florida (Carlisle et al., 1978). This report contains characterization data for a Lakeland sand.

The properties that were selected to represent the soil profile of the experimental site are summarized in Table 5.1. The average depth to the restricting layer for the three wells within the application area is 2.62 m and this was chosen to represent the profile depth.

Table 5.1 Soil properties used in simulations.[1]

Depth (cm)	Organic Carbon (%)	Bulk Density (g/cm^3)	Hydraulic Conductivity (cm/hr)	Water Content (%)		
				Effective Saturation	Field Capacity[2]	Wilting Point[3]
0- 13	0.55	1.45	13.3	33.0	10.0	2.1
13- 20	0.28	1.60	13.3	33.0	10.0	2.1
20- 51	0.08	1.58	22.9	33.3	10.0	2.1
51-102	0.04	1.59	36.5	33.8	9.0	2.1
102-262	0.03	1.59	45.0	34.0	9.0	2.1

[1]Data from Hook (1985) and Carlisle, et al., (1978).
[2]Field gravimetric water content following 48 hours of drainage under plastic following 16 hours of flooding.
[3]Water content at 15 bars tension.

5.1.3 Pesticide chemical properties and applications

The pesticide chemical properties required by the models are solubility, partition coefficient, degradation rates on foliage and in the soil, and a coefficient of plant uptake. The models may require these parameters in slightly different forms, but the basic information required is the same. In addition to the model manuals, the manual for LEACH (Dean et al., 1984) was a good source of estimates of the required parameters. No exhaustive search of possible values of parameters for each chemical was undertaken. At this point in the study, the models were run using values that a user could obtain from the manuals. This may result in less than optimum performance of the models, but probably reflects the way in which a typical user would apply them.

Reported properties of pesticides are often widely variable. For properties such as partition coefficient and degradation rates, the

variability is understandable and expected. However, even water solubility was found to vary by a factor of two. The solubility of atrazine is not available from the PRZM manual. The CREAMS manual lists a value of 33 mg/L. However, the Agrichemical Handbook (1983) gives a value of 70 mg/L at 20°C. The solubility of alachlor is given in the PRZM manual as 220 mg/L at 20-25°C. The CREAMS manual reports a value of 242 mg/L at an unspecified temperature. The Farm Chemical Handbook (1984) does not report a value for alachlor and the Agrichemical Handbook (1983) gives the solubility of alachlor in water as 148 mg/L at room temperature. The final values selected for all chemical properties are shown in Table 5.2.

The solubilities of bromide, nitrate, and chloride listed in Table 5.2 are considerably less than the actual solubilities. However, solubilities of ionic species are seldom listed for reference. The values in Table 5.2, while less than the actual solubility values, are sufficiently high such that solubility was not a limiting factor in the mobility of the chemicals.

Table 5.2 Chemical properties used in simulations.

Property	Atrazine	Alachlor	Bromide	Nitrate	Chloride
Solubility (mg/L)	33	148	800	800	800
Partition coef., K_{oc} (cm^3/g)	163	268	0	0	0
Half-life (days)	78	18	999	999	999
Plant Uptake Coef.	1.0 0.65 0.0	1.0 0.52 0.0	1.0 0.0	1.0 0.0	1.0 0.0

The user manuals for the models contain tables drawn from many sources which provide values of the partition coefficient for many pesticides. The LEACH manual also contains a number of tables. The tables in CREAMS and LEACH are more extensive than those in PRZM. Different tables within the same manual may give differing values. Table values often list coefficients of variation (CV) on the order of 50-130 percent. PRZM presents equations by which the organic carbon partition coefficient, K_{OC}, can be calculated if solubility or the octanol-water partition coefficient, K_{OW}, is known.

The partition coefficients of alachlor and atrazine were not measured on this soil and thus values were chosen from the sources described above. A K_{OC} value for atrazine of 163 cm^3/g with a CV of 49% was found in the LEACH manual. No listing of a K_{OC} was found for alachlor. PRZM did list a value for $\log(K_{OW})$ which was 2.78. PRZM presents a relationship between $\log(K_{OW})$ and K_{OC} which is

$$\log K_{OC} = 1.00 \ (\log K_{OW}) - 0.21 \qquad 5.1$$

Using this equation a K_{OC} of 371 was calculated for alachlor. LEACH lists a K_{OW} value for alachlor as 434, using this and equation 5.1, a K_{OC} value of 268 was calculated. Since alachlor has been reported as one of the pesticides commonly found in groundwater, it was decided to choose the lower K_{OC} value for use in the model as this would tend to cause higher predicted leaching losses.

The inorganic tracers bromide, chloride, and nitrate were assumed to act as non-adsorbed pesticides. Thus they were assigned a K_{OC} value of zero.

The degradation rate constant of atrazine in soil was given in the LEACH manual as ranging from 0.0149 to 0.0063 $days^{-1}$, corresponding to a half-life of between 46 and 110 days respectively. The midpoint value of 78 days was chosen for use in these simulations. A degradation rate constant of 0.0384 $days^{-1}$, which corresponds to a half-life of 18 days, was given for alachlor in both the CREAMS and LEACH manuals.

The coefficient of plant uptake of pesticides with transpiration was determined using the relationship given in the PRZM manual in which the uptake factor is a function of K_{ow} and is given as

$$UPTKF = 0.784 \exp - [(\log K_{ow} - 1.78)^2/2.44] \qquad 5.2$$

where UPTKF = plant uptake efficiency factor.

Using the K_{ow} for alachlor of 434 as discussed above, the uptake factor was calculated to be 0.52. Back calculating a K_{ow} for atrazine, based upon the chosen K_{oc} of 163 using equation 5.1, yields a K_{ow} of 264. Using this value in equation 5.2 gives a plant uptake factor of 0.65.

The models were also run using uptake factors for both atrazine and alachlor of 0.0 and 1.0 in order to assess the sensitivity to these factors. GLEAMS currently recommends that in the absence of well defined uptake coefficients, a value of 1.0 should be used. Uptake factors for the inorganic tracers were assigned values of both 0.0 and 1.0 to observe the sensitivity of these non-adsorbed chemicals to plant uptake.

The dates and amounts of the chemicals applied to the soil surface of the experimental site were entered into the models in a direct manner, ie. there were no calculations or transformations required to convert the actual values into model parameters. The application rates used in the simulations correspond to the intended application rates as opposed to

the measured rates. The dates and application rates used as model inputs are shown in Table 5.3. The applications were assumed to reach the soil surface with no chemical residues remaining on plant surfaces. The amount applied was further assumed to be uniformly incorporated into the top 1 cm of the soil.

5.1.4 Length of simulations

Both models simulated the two year time period from 1/1/86 through 12/31/87. This was done to allow the models to overcome any effects of initial conditions prior to beginning simulation of chemical applications. Continuing simulations for six months beyond the end of field data collection would show if any significant leaching would likely have occurred after sampling was terminated.

Table 5.3 Chemical applications summary.

Date	Chemical Applied	Application Rate (kg/ha)
11/12/86	Atrazine	4.9
	Alachlor	4.9
11/17/86	Bromide	10.0
4/16/87	Nitrate	18.6
4/27/87	Bromide	17.0

5.2 Parameters Unique to PRZM

5.2.1 Evapotranspiration prediction.

PRZM uses either measured daily pan evaporation or daily mean temperature to determine evaporation from the soil and plant surfaces, and transpiration by the crop. In these simulations, daily pan

evaporation values recorded at a weather station located on the University of Georgia Coastal Plain Experiment Station campus were used. This weather station is located approximately 8 km from the research site. PRZM requires a pan coefficient which is a multiplier used to adjust pan readings to represent total daily potential evapotranspiration (PET). A pan factor of 0.75 was selected from a figure provided in the manual showing pan factors as related to geographic location.

Two additional parameters required for evapotranspiration (ET) prediction are the depth in the soil profile from which evaporation can occur, and the depth of rainfall and irrigation that can be stored on the plant canopy (interception storage). A figure in the manual indicates that for southern Georgia, the depth of soil contributing to evaporation is approximately 25 cm. Data pertaining to the interception storage capacity of bahia grass was not included in the manual. Values presented in the manual for various crops ranged from 0.0-0.3 cm. Assuming that the storage capacity of bahia grass is relatively small, a value of 0.05 cm was assumed.

5.2.2 Crop related parameters

Characteristics of the crop(s) grown during the simulation period are defined by parameters related to rooting depth, maximum canopy coverage, and dates for emergence, maturation, and harvest. A rooting depth for bahia grass was difficult to obtain. Most references to bahia grass simply stated that it is a deep or very deep rooted plant. Based on such generalizations and without more specific information, an active rooting depth (depth containing 90% of root mass) of 91 cm (3 ft) was

selected. Based on observations at the research site, a maximum areal coverage of the bahia grass foliage was estimated as 98 percent.

Dates of crop emergence, maturation, and harvest are used in the model to define the development and growth of roots. Roots are assumed to begin growing at crop emergence and reach the maximum rooting depth at plant maturation. The roots stay at maximum depth until harvest when they are set back to zero. These parameters are somewhat difficult to define in relation to a perennial crop such as bahia grass. In view of the use made of the selected dates, some artificial dates for emergence and harvest could be selected. Since the emergence date really defines the beginning of plant transpiration as a component of the water balance, an emergence date of March 1 was selected to correspond to the time when the grass begins to "green up" in the spring. Since the majority of the roots already exist when the grass begins active growth in the spring, a maturation date of April 1 was selected to reflect water extraction from the full maximum rooting depth shortly after growth for the new year begins. The harvest date was chosen to be December 1 which reflects the approximate date when the grass turns brown in the winter and active growth ceases.

5.2.3 Soil related parameters

PRZM will allow simulation of a larger section of the profile than just the root zone. A soil core depth of 2.62 m was chosen to represent the average profile depth beneath the application area. The model will allow the user to select the number of compartments used to represent the profile. Too many compartments will increase simulation times and too

few will lead to increased numerical errors in the solution of the equations used within the model. The manual suggests that no fewer than 30 compartments be used. Thirty-five compartments were selected because this gives a compartment depth that is one-half the compartment depth in GLEAMS for a root zone depth of 91 cm (see section 5.3.3).

PRZM and GLEAMS both normally operate on the assumption that any soil water in excess of field capacity will drain into the next lower compartment. This drainage will continue until any excess water drains from the bottom of the simulated profile. This drainage is assumed to occur within one day. In the PRZM model, this type of drainage is called 'free drainage'. PRZM has a feature to allow selection of a drainage rate parameter that serves to slow down the percolation process. This is an empirical constant and requires calibration. A figure is provided in the manual whereby the user can make a first cut selection of the drainage parameter based upon the soil type (sand, clay loam, etc.) and the number of simulation compartments selected as described above. Observations at the experimental site clearly show that there is a delay of 2-4 days from the time excess water is applied to the time that the water table responds. Therefore a few simulations were made using the restricted drainage option to compare with the experimental data. The drainage rate parameter for this case was selected from the graph in the manual for a sand soil with 35 compartments to be 2.63 day^{-1}.

5.3 Parameters Unique to GLEAMS

5.3.1 Evapotranspiration prediction

Potential evapotranspiration (PET) is computed in GLEAMS based on mean monthly maximum and minimum temperatures and mean monthly solar radiation. The mean monthly temperatures and solar radiation data were obtained from the same weather station that was used for the pan evaporation data input to PRZM (section 5.2.1). GLEAMS also differentiates between soil evaporation and plant transpiration. A soil evaporation parameter is required as a model input and the manual gives a suggested value of 3.3 (no units) for this parameter for sands.

5.3.2 Crop related parameters

Crop related parameters which are different from PRZM are leaf area index (LAI), and winter cover factor. The LAI data are used to reflect changes in plant transpiration with stage of growth. In keeping with the observed behavior of bahia grass discussed in section 5.2.2, the LAI of bahia grass was assumed to be zero until March 1 of each year and to return to zero on December 1st. The maximum LAI for bahia grass was assumed to be similar to the LAI for pasture as presented in the CREAMS manual which had a maximum LAI of 3.0. The LAI for the bahia grass was assumed to reach 2.0 on April 1 and to reach 3.0 May 1 where it remained until it began to decline again to a value of 2.0 on Nov. 1.

The winter cover factor is used to moderate evaporation from the soil surface during the winter due to presence of a bare surface or cover crops. Since the soil surface at the site was not bare during winter, the recommended value of the winter cover factor of 0.5 was used.

5.3.3 Soil related parameters

GLEAMS was designed to simulate only the root zone of a crop. The vadose zone below the crop is ignored. Thus, the soil profile description input to GLEAMS covers only the 91 cm root zone as opposed to the 2.62 m profile input to PRZM. There are no soil parameters which are significant to the results presented in this work which differ from those discussed in section 5.1.2. In order to highlight one of the major differences between the two models, a short discussion of the computational layering of the soil profile in GLEAMS will be presented here. GLEAMS divides the crop root zone into seven computational layers. The first layer is defined to be 1 cm in depth and the other 6 layers are equal in thickness (layer 2 is 1 cm less than layers 3-7) and together account for the rest of the root zone. The 1 cm upper layer is considered an important feature of CREAMS and GLEAMS because it increases the sensitivity of erosion and runoff to chemical concentrations near the soil surface. PRZM divides the entire profile into a specified number of compartments of equal depth. For the case presented here, GLEAMS layers would be 15 cm thick after the surface layer (91 cm / 6 layers). For PRZM with a 2.62 m profile and 35 compartments, each compartment will be 7.5 cm thick. Thus, PRZM may be better able to describe effects of actual soil layering since properties of adjoining layers would not be averaged over as large a layer as in GLEAMS. However the surface layer in PRZM will also be 7.5 cm thick and pesticide storages will be averaged over this whole layer effectively lowering the mass at the surface which is available for transport with eroded sediment and runoff water.

CHAPTER 6
RESULTS AND DISCUSSION

There are many areas in this study for which results can be reported. The approach used in this chapter is to report significant results relative to each area such as sample collection, sample analysis, simulation results, etc., and then relate the individual results where appropriate. A summary of activities at the field site is presented in Table 6.1 for reference.

6.1 Data Collection

The site was visited on at least a weekly basis throughout the study. At each visit, samples were collected from the monitoring wells and soil solution samplers. The water table elevation was also recorded for every monitoring well on the site and for several wells located adjacent to the study area. Soil samples were collected on an irregular basis during the study.

The procedure used for collecting samples from the groundwater worked well in general. Sand intrusion into a few of the wells, however, was a consistent problem. It was possible in some instances to fill the 250 mL sampling bottle with sand. This problem was overcome by slowly raising the bottom of the sampling tube in order to stay above the sand. These wells were pumped out using a 1.6 cm diameter suction line to remove accumulated sand as needed. The problem could have been avoided

Table 6.1 Chronological summary of field site activities.

Date	Event
11/12/86	Apply 4.9 kg/ha of atrazine and alachlor, apply 5.1 cm of irrigation after herbicide application.
11/17/86	Apply 500 g of KBr (10 kg/ha Br^-), collect soil solution samples.
11/18/86	Collect soil solution samples. First soil samples taken from top 5 cm in application area.
11/24/86	Collect soil solution and soil samples.
12/01/86	Collect soil solution samples.
12/08/86	Collect soil solution samples, apply 5.1 cm of irrigation.
12/15/86	Collect soil solution and well samples.
12/22/86	Collect soil solution, well, and soil samples.
12/29/86	Collect soil solution and well samples.
1/05/87	Collect soil solution and well samples.
1/12/87	Collect soil solution and well samples.
1/19/87	Collect soil solution and well samples.
1/26/87	Collect soil solution and well samples.
2/02/87	Collect soil solution and well samples.
2/09/87	Collect soil solution, well, and soil samples.
2/16/87	Collect soil solution and well samples.
2/23/87	Collect soil solution and well samples.
3/02/87	Collect soil solution and well samples.
3/09/87	Collect soil solution and well samples.
3/16/87	Collect soil solution, well, and soil samples.

Table 6.1 Continued.

Date	Event
3/23/87	Collect soil solution and well samples.
3/31/87	Collect soil solution and well samples.
4/06/87	Collect soil solution and well samples.
4/13/87	Collect soil solution and well samples.
4/16/87	Apply 560 kg/ha of 5-10-15 to entire study site.
4/20/87	Collect soil solution and well samples, Very few wells have water.
4/27/87	Collect soil solution and well samples, Apply 2.5 cm of irrigation, apply approximately 17 kg/ha Br^-, apply 2.5 cm of irrigation.
4/28/87	Collect soil solution and well samples, apply 4.2 cm of irrigation.
4/29/87	Collect soil solution and well samples, apply 3 cm of irrigation.
4/30/87	Collect soil solution and well samples, apply 3 cm of irrigation.
5/01/87	Collect soil solution and well samples, pour 10 l of solution containing 500 g KCl into well 07-09, apply 2.7 cm of irrigation.
5/02/87	Collect soil solution and well samples, apply 3.2 cm of irrigation.
5/03/87	Collect soil solution and well samples, apply 1.9 cm of irrigation.

Table 6.1 Continued.

Date	Event
5/05/87	Collect soil solution and well samples, apply 0.9 cm of irrigation.
5/08/87	Collect soil solution and well samples, apply 1.9 cm of irrigation.
5/11/87	Collect soil solution and well samples, apply 5.2 cm of irrigation.
5/13/87	Collect soil solution and well samples.
5/18/87	Collect soil solution and well samples.
5/25/87	Collect soil solution, well, and soil samples.
6/01/87	Collect soil solution and well samples.

by using commercially available PVC well screening in the monitoring wells.

No problems were observed with the operation of the soil solution samplers. The volumes of water collected during sampling varied from 0 to greater than 50 mL. Even though the samples were pulled back to the instrument trailer through as much as 35 m of 0.64 cm ID polypropelene tubing, the vacuum applied to the sample lines was sufficient to pull very small droplets of water along the wall of the tube and into the containers. No carryover of the tracers between sampling periods was observed.

The tensiometers were difficult to maintain properly on the weekly sampling schedule. Even when the tensiometers were working, their usefulness was limited by the short length of time during which they

could be observed. If an irrigation was initiated early in the morning, a few of the 30 cm tensiometers might have responded by the end of the day. Weekly observations of soil-water tension were insufficient for the purpose of calculating the flux of water through the unsaturated zone.

6.2 Sample Analysis

Water samples collected from the monitoring wells were analyzed for residues of atrazine and alachlor and concentrations of the inorganic tracers utilized in this research (Br^-, NO_3^-, and Cl^-). The volume of samples from the solution samplers ranged from 0 to more than 50 mL, with the average sample volume being approximately 10 mL. Water samples from the soil solution samplers were generally analyzed for the inorganic tracers only. Most of the solution samples were not extracted for residues of the herbicides due to the small sample volumes. Approximately 50 of the soil solution samples were extracted and analyzed for residues of the herbicides. Soil samples were extracted and analyzed for residues of atrazine and alachlor. The presence of alachlor and atrazine residues in the soil samples was confirmed in a composite of soil sample extracts that was analyzed using gas chromatography/mass spectrometry (GC/MS).

During extraction of water samples with hexane, an emulsion of hexane and water sometimes formed. This would usually separate if allowed to sit undisturbed for a few minutes. If the emulsion did not separate, herbicide residues contained within the emulsion could have been discarded. There was an apparent contamination of the glassware used for water sample collection or extraction. Samples of deionized

water were extracted and they showed concentrations of atrazine of approximately 1 μg/L. All glassware was routinely washed with a commercial glassware detergent, triple rinsed with deionized water, and rinsed with acetone. The contamination levels appeared to be consistent in that water samples, in which atrazine was not expected, showed a concentration of approximately 1 μg/L. The source of the contamination was not determined. Several attempts were made to isolate and identify the source of the contamination, however these attempts were unsuccessful. To account for the contamination, the measured concentrations were reduced by 1 μg/L. Thus no concentrations of less than 1 μg/L are reported even though the sensitivity of the GC would allow detection down to the range of tenths of a μg/L.

The gas chromatograph performed well except that the N-P detector response had a tendency to drift. This was accounted for by running standards frequently and adjusting calculated concentrations as described in the methods section.

The recoveries of atrazine and alachlor from spiked water samples were nearly identical and ranged from 68 to 104% with a mean of 79% and a standard deviation of 12 percent. The standard deviation would probably be reduced if these analyses had been performed by an experienced analyst. Experience contributes significantly to the ability to produce accurate and consistent results.

The recoveries of atrazine and alachlor from spiked soil samples could not be determined from the data collected. Moisture contents of the soils used for spiking were not recorded. The spike levels were based on the moist weight of the soil. After spiking, the soil was air-

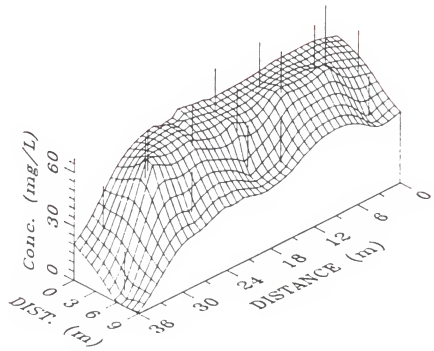
dried for 1 day in order to allow the solvent from the herbicide standards to evaporate prior to taking subsamples for analysis. The loss of water from the samples during this time resulted in an increased mass of pesticide per unit weight of wet soil. Since the initial moisture contents were unknown, it was not possible to calculate the expected concentrations in the air dried samples. Calculations based on the spiking levels of the moist soil resulted in apparent recoveries that exceeded 100 percent. It can be concluded from the data that recoveries from the soil were high. When the omissions in the soil recovery study were discovered, the facilities used to perform extractions and analyses were no longer available.

All concentrations (water and soil) reported in the following sections are the analytically determined concentrations and have not been adjusted for expected recovery rates.

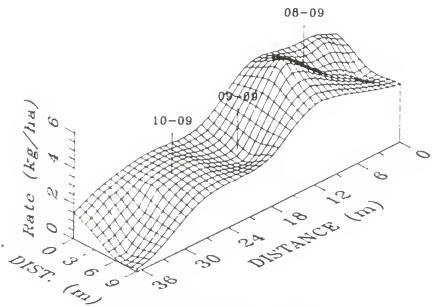
6.3 Chemical Applications

Applications of the herbicides and bromide tracer were monitored to determine the concentration of the chemicals in the application water and the volume of water applied. Concentrations of the chemicals were multiplied by the volume of water collected and divided by the opening area of the collectors in order to determine the application rate on a mass per unit area basis. Table 6.2 summarizes the measured chemical application data. The intended application rates were presented in Table 5.3.

The application of atrazine and alachlor to the designated application area was not uniform as can be seen in Figures 6.1 and 6.2.



a) Solution Concentration



b) Application Rate

Figure 6.1. Uniformity of atrazine application, a) concentration in application solution (vertical bars show sampling locations), b) application rate (vertical bars show location of monitoring wells)

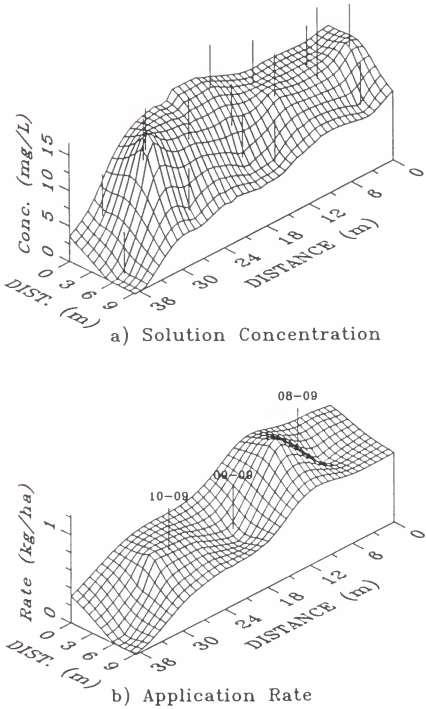


Figure 6.2. Uniformity of alachlor application, a) concentration in application solution (vertical bars show sampling locations), b) application rate (vertical bars show location of monitoring wells)

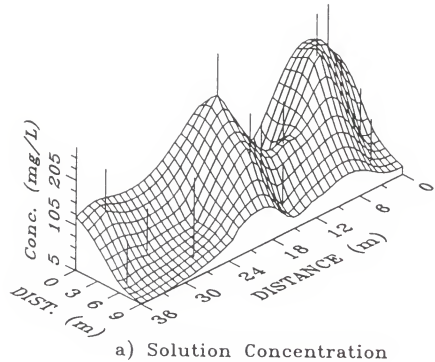
The application solution was used up just as the sprayer crossed over well 10-09 (6.1 m short of intended end of application) causing the rapid decrease in application rate at that point. Overall, the application showed considerable variability that is probably representative of chemical applications in general. Similar nonuniformity was observed during the second application of the bromide tracer as shown in Figure 6.3. The samples taken during the first application of bromide were lost due to inadvertent freezing of the samples and subsequent breakage of the glass sample containers.

Table 6.2 Chemical application results.

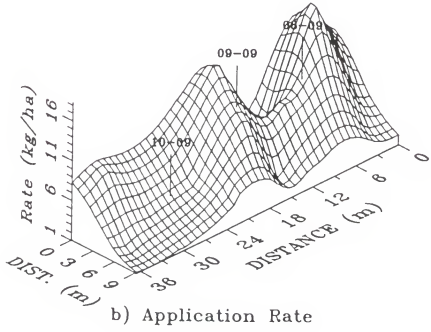
Date of Application	Chemical	Depth of Water (cm)[1]	Concentration (mg/L)[1]	Application Rate (kg/ha)[1]
11/12/86	Atrazine	0.70	51.5	3.41
		(31)[2]	(28)	(39)
11/12/86	Alachlor	0.70	11.1	0.72
		(31)	(34)	(36)
11/17/86	Bromide (from KBr)	0.86	-[3]	-[3]
		(20)		
4/27/87	Bromide (from KBr)	0.74	111.0	7.47
		(20)	(87)	(75)

[1]Mean of observations
[2]Coefficient of variation (%)
[3]Samples lost prior to analysis.

The nonuniformity of application demonstrates one of the problems associated with prediction of chemical transport within the soil profile. In addition to recognized variability of soil properties, there is the compounding influence of variability in application rates over a field. The concentrations of alachlor measured in the application samples were



a) Solution Concentration



b) Application Rate

Figure 6.3. Uniformity of bromide application on 4/27/87, a) concentration in application solution (vertical bars show sampling locations), b) application rate (vertical bars show location of monitoring wells)

significantly lower than for atrazine although they were applied at the same rate (4.9 kg/ha). Figure 6.4 shows the relationship between measured concentrations of alachlor and atrazine in the sample collection containers. The concentration of alachlor in a container is strongly correlated to the concentration of atrazine. The alachlor concentrations were, in general, only about 24% of the atrazine concentrations. Soil sample data taken six days after application (Table 6.3) suggests that more alachlor reached the soil than indicated by the application rate shown in Table 6.2. Possible explanations for the concentrations of alachlor in the application samples include errors in formulating the application solution, adsorption to the plastic cup, and volatilization.

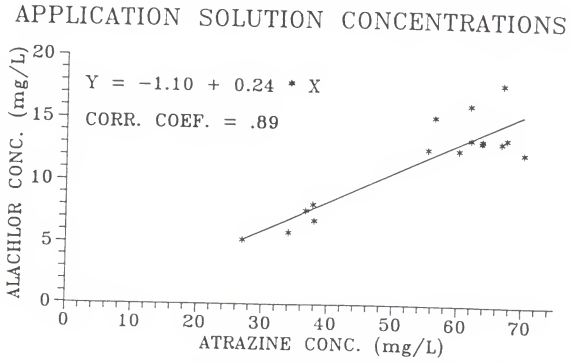


Figure 6.4. Comparison of alachlor and atrazine concentrations in application samples.

Alachlor is more volatile than atrazine. However, these samples were exposed for less than 10 minutes after the application (while being collected, sealed in glass containers, and placed on ice).

6.4 Chemicals in the Unsaturated Zone

6.4.1 Atrazine and Alachlor

Samples of the top 5 cm of soil were taken from 14 locations within the application area on 11/18/86, which was six days after application. Five cm of irrigation water had been applied prior to this sampling. Table 6.3 compares the measured application rates of atrazine and alachlor shown in Table 6.2 with the average measured soil concentrations on this date. A simple calculation reveals that if the actual application rate of alachlor was 0.72 kg/ha and was entirely contained within the top 5 cm of soil, the maximum possible concentration in the soil would be approximately 1 mg/kg (assuming that the soil bulk density equals 1.45 g/cm^3). The 3.41 mg/kg measured average value could

Table 6.3 Measured application rates and soil surface concentrations of atrazine and alachlor.

	Atrazine	Alachlor
Application rate (kg/ha)	3.41[1] (39)[2]	0.72 (36)
Soil Concentration (mg/kg)	0.29 (68)	3.26 (58)

[1]Mean [2]Coefficient of variation (%)

only be achieved if the actual application rate were at least 2.5 kg/ha. If the planned application rate of 4.9 kg/ha were contained within the top 5 cm of soil, the expected concentration in the soil would be 6.75 mg/kg. The observed soil concentrations suggest that the alachlor in the application samples either volatilized rapidly or adsorbed to the collection containers prior to transfer into glass containers. If volatilization from the sample containers was the reason for the low concentrations, it would be expected that there would also have been significant volatilization from the grass foliage and soil surface prior to irrigating the site and moving the chemical off of the foliage and into the soil profile.

The low concentration of atrazine within the top 5 cm of soil is probably due to movement below this depth with percolating water before collection of these samples. Soil samples collected six days later (11/24/86) showed considerably more atrazine in the zone from 5 to 15 cm than from 0 to 5 cm. Samples from the 5-15 cm depth range were not collected on November 18.

Figures 6.5 and 6.6 show the relationship between the measured soil concentration of atrazine in the top 5 cm of soil on 11/18/86 and the concentration of the application solution and the application rate, respectively. Figures 6.7 and 6.8 show the same relationships for alachlor. Figure 6.5 shows that there was a poor correlation between the concentration of the application solution and the concentration in the upper 5 cm of soil measured at the same locations 6 days after application. Figure 6.6 shows that there was a higher correlation between application rate and the soil concentration than there was for

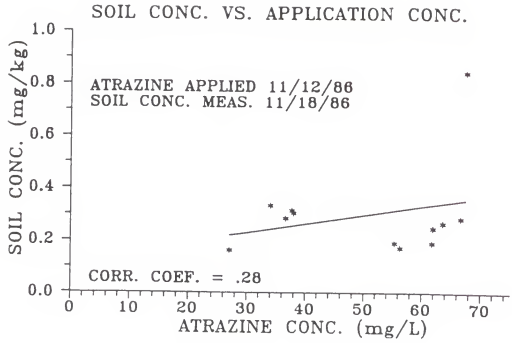


Figure 6.5. Correlation between atrazine concentrations in the top 5 cm of soil and application solution concentrations.

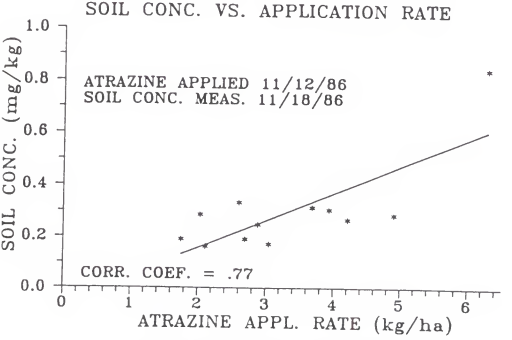


Figure 6.6. Correlation between atrazine concentrations in the top 5 cm of soil and application rate.

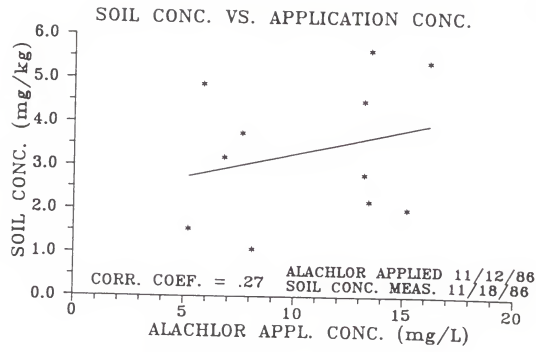


Figure 6.7. Correlation between alachlor concentrations in the top 5 cm of soil and application solution concentrations.

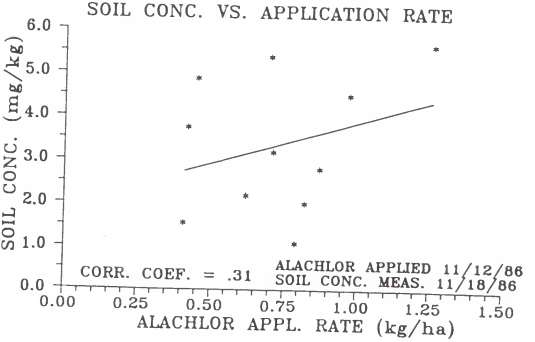


Figure 6.8. Correlation between alachlor concentrations in the top 5 cm of soil and application rate.

application solution concentration and soil concentration. Figures 6.7 and 6.8 show that there was essentially no correlation between either alachlor concentration in the application solution or application rate and the concentration of alachlor in the top 5 cm of soil.

Additional soil samples were collected four more times during the study. In order to reduce the total number of samples collected, the number of depths sampled was increased and the number of sampling locations was decreased with each successive sampling date. Alachlor was not observed to move below a depth of 36 cm in the soil. No trace of alachlor was detected in the shallow groundwater samples. Consequently, most of the results discussed in subsequent sections will be limited to atrazine. Results of soil sample analyses for atrazine and alachlor residues are presented in Tables 6.4 and 6.5, respectively. Table 6.4 shows that the sampling strategy to increase the depth of sampling with time since application resulted in missing the passage of the initial atrazine front past any point. Samples from a depth of 178-188 cm on 12/22/87 already showed atrazine residues. Tables 6.4 and 6.5 include a calculation of the total mass of atrazine and alachlor in the soil profile beneath the application area, respectively. For these calculations, the concentration was assumed to vary linearly between sample points. The concentration of atrazine within the profile appears to increase with time for the first 4 sampling dates due to the way in which the samples were collected (increasing depth of sampling over time. The maximum mass of atrazine within the soil profile was calculated to be 70 g on 2/9/87 which is approximately 47% of the intended application of 150 g, or 62% of the measured application

Table 6.4. Mean concentrations of atrazine (mg/kg) in soil samples.

Sample Depth (cm)	Sample Date					
	11/18/86	11/24/86	12/22/86	2/9/87	3/16/87	5/25/87
0-5	0.29[1] (68)[3]	0.23 (61)	NS[2]	NS	0.06 (42)	NS
0-15	NS	NS	NS	0.16 (53)	0.15 (29)	0.04 (15)
5-15	NS	0.55 (47)	NS	NS	NS	NS
25-36	NS	NS	0.11 (45)	0.23 (61)	0.13 (51)	0.07 (20)
41-51	NS	NS	NS	0.15 (30)	0.08 (71)	NS
56-66	NS	NS	0.02 (45)	0.09 (49)	0.05 (65)	0.04 (78)
71-81	NS	NS	NS	0.05 (53)	NS	NS
86-97	NS	NS	0.02 (63)	0.04 (40)	0.03 (94)	0.03 (61)
117-127	NS	NS	NS	0.03 (58)	0.03 (125)	NS
132-142	NS	NS	0.02 (49)	NS	NS	0.02 (31)
147-157	NS	NS	0.01 (77)	NS	0.02 (38)	NS
178-188	NS	NS	0.01 (64)	NS	0.04 (67)	0.01 (38)
Calculated Mass in Profile (g)	7	32	40	70	58	32

[1]Mean [2]No Sample [3]Coefficient of variation (%)

Table 6.5. Mean concentrations of alachlor (mg/kg) in soil samples.

Sample Depth (cm)	Sample Date					
	11/18/86	11/24/86	12/22/86	2/9/87	3/16/87	5/25/87
0-5	3.26 (58)	3.11 (59)	NS	NS	1.67 (55)	NS
0-15	NS	NS	NS	0.73 (104)	0.68 (23)	0.12 (65)
5-15	NS	0.17 (96)	NS	NS	NS	NS
25-36	NS	NS	0.00	0.00	0.02 (224)	0.01 (141)
Calculated Mass in Profile (g)	79	84	0	53	69	13

[1]Mean [2]No Sample [3]Coefficient of variation (%)

rate of 3.41 kg/ha over an application area of 334 m^2 (114 g). The maximum mass of alachlor within the soil profile was calculated to be 79 g on 11/18/86. This represents 53% of the intended application rate, and in excess of 300% of the calculated application rate based on the collection of the application solution as described above.

The complete data set of soil sample concentrations can be provided upon request. Refer to Appendix B for information on how to request the data and a sample of the data set.

Approximately 30 samples from the soil solution samplers were extracted and analyzed for residues of atrazine and alachlor. The samples from sampler 09N-2 showed a pulse of atrazine moving past the 61 cm depth. The peak concentration of atrazine in samples from this sampler was approximately 0.35 mg/L and this peak occurred on Nov. 24,

1986, which was 16 days after application. A plot of the atrazine and bromide concentrations, from these samples, as a function of the total depth of water applied since application of each chemical is presented in Figure 6.9. Since the bromide was applied 5 days after the atrazine, the concentrations were plotted as a function of the total water applied since each chemical was applied to provide a common base for comparison. From this figure it can be seen that approximately 2.4 times as much water had to be applied to move the peak concentration of atrazine past the 61 cm depth as was required to move the bromide peak past the same point. This can be interpreted as an approximation of the retardation factor of atrazine in this soil (assuming that the bromide

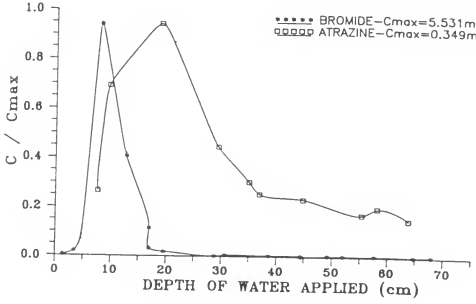


Figure 6.9. Bromide and atrazine concentrations in solution sampler 09N-2 as a function of total water applied since application.

tracer is nonadsorbed). The retardation factor can be written as

$$R = 1 + \frac{(K_d)(\rho_b)}{\theta_{fc}}$$

where R = retardation factor, dimensionless, K_d = partition coefficient, ρ_b = soil bulk density, and θ_{fc} = soil-water content at field capacity (Dean et. al, 1984). The retardation factor indicates the velocity of water or a nonadsorbed chemical relative to the velocity of an adsorbed chemical. Thus a retardation factor of 2 would indicate that the adsorbed chemical would move at 1/2 of the velocity of a nonadsorbed species.

Using the soil properties listed in Table 5.1 and a normalized partition coefficient for atrazine of 163 cm^3/g), a weighted average retardation factor for the top 61 cm of the soil profile was calculated to be approximately 6. The properties listed for the top 13 cm yield a retardation factor of 14 and the properties of the layer from 51-62 cm give a retardation factor of 2.

Alachlor was not detected in any of the extracted soil solution samples.

6.4.2 Bromide

The concentrations of bromide (Br^-) in the 61, 122, and 183 cm deep solution samplers following the first application of bromide to the site are shown in Figures 6.10-6.12, respectively. The first application of bromide was made 5 days after the application of atrazine and alachlor. The date of the application of the herbicides to the application site (11/12/86) is used as the benchmark time to which all observations and

results are referenced. These figures demonstrate the observed variability between sampling locations. Figure 6.13 shows the average concentration, from the 6 sampling locations, of bromide at each sample depth following the first bromide application. Figures 6.14-6.16 show the concentrations of bromide following the second application in the 61, 123, and 183 cm solution samplers, respectively. Again, the variability between sampling locations is evident. Figure 6.17 shows the average concentration of bromide at each sample depth following the second bromide application.

Tables 6.6 and 6.7 present the mean concentrations and coefficients of variation between sampling locations of bromide at each sampling depth on selected sampling dates following the first and second applications of bromide, respectively. These tables show that the coefficient of variation between sampling locations ranges from 23 to over 200%.

The results of all analyses for tracers and herbicides in both soil and water samples can be provided on magnetic media. Refer to Appendix B for information on how to request this data and a sample of the data sets.

6.4.3 Nitrate

The entire field was fertilized on 4/16/87 at a rate of 560 kg/ha of 5-10-15. Concentrations of nitrate (as NO_3) moving through the vadose zone following the fertilizer application exhibited extreme variability. There were virtually no detections of nitrate due to the fertilizer application in the samplers located at a 61 cm depth. Two samplers located at a depth of 122 cm showed a response to the fertilizer

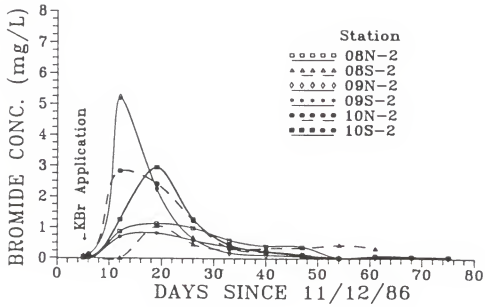


Figure 6.10. Bromide concentration for six sampling locations following the first application at a 61 cm depth.

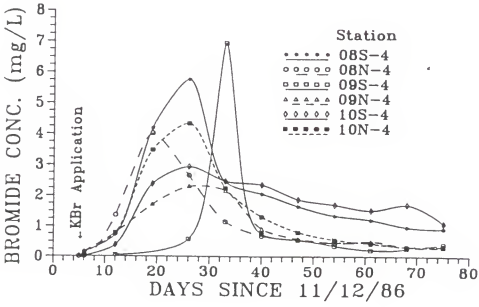


Figure 6.11. Bromide concentration for six sampling locations following the first application at a 122 cm depth.

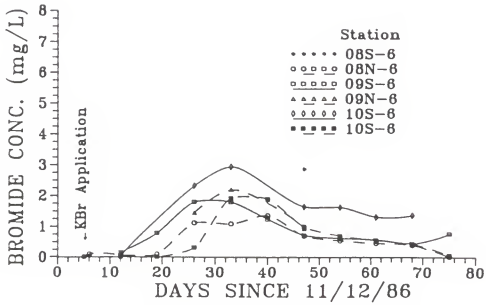


Figure 6.12. Bromide concentration for six sampling locations following the first application at a 183 cm depth.

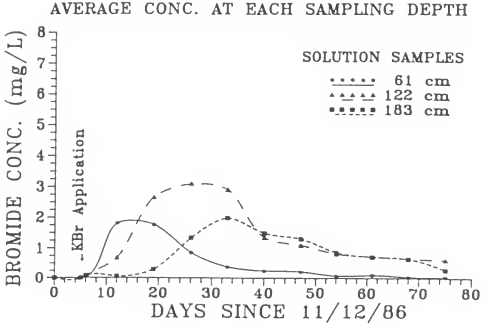


Figure 6.13. Average bromide concentration for the three sampling depths following the first application.

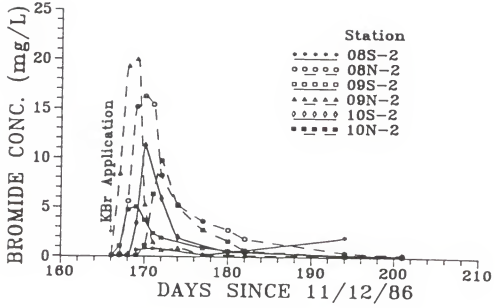


Figure 6.14. Bromide concentration for six sampling locations following the second application at a 61 cm depth.

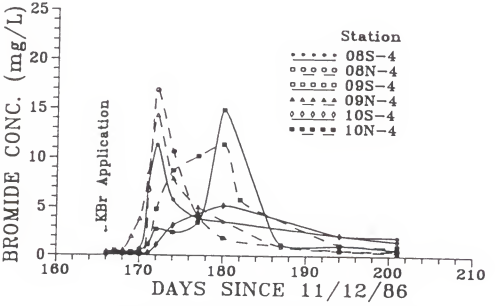


Figure 6.15. Bromide concentration for six sampling locations following the second application at a 122 cm depth.

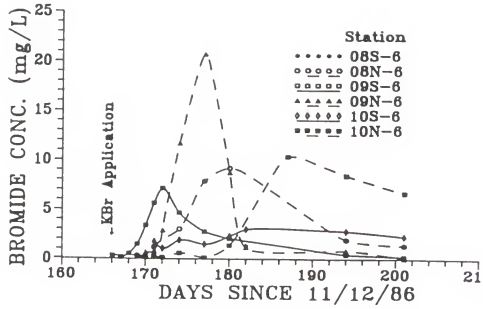


Figure 6.16. Bromide concentration for six sampling locations following the second application at a 183 cm depth.

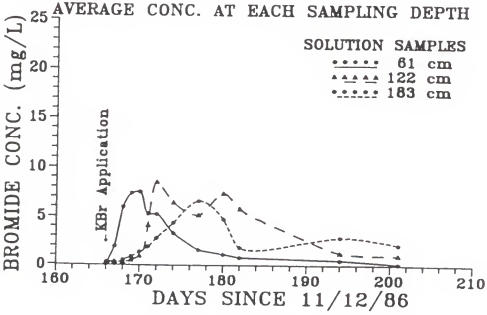


Figure 6.17. Average bromide concentration for the three sampling depths following the second application.

Table 6.6. Mean concentration of bromide (mg/L) at each sampling depth following first application[1].

Sample Date	Sample Depth (cm)		
	61	122	183
11/17/86	0.03[2] (115)[3]	0.00 (0)	0.00 (*[4])
11/18/86	0.05 (114)	0.10 (82)	0.10 (*)
11/24/86	1.92 (106)	0.72 (65)	0.05 (135)
12/01/86	1.87 (50)	3.35 (34)	0.31 (146)
12/08/86	0.90 (41)	3.28 (58)	1.48 (54)
12/15/86	0.39 (41)	3.07 (71)	2.10 (34)
12/22/86	0.25 (45)	1.42 (53)	1.58 (23)
12/29/86	0.22 (63)	1.15 (58)	1.37 (65)
01/05/87	0.08 (225)	0.85 (70)	0.91 (59)
01/12/87	0.11 (96)	0.75 (71)	0.75 (56)
01/19/87	0.04 (65)	0.68 (89)	0.68 (73)
01/26/87	0.04 (44)	0.65 (58)	0.29 (156)
02/02/87	0.09 (156)	0.52 (78)	0.51 (60)
02/09/87	0.12 (191)	0.45 (65)	0.67 (81)

[1]Bromide applied 11/17/86
[2]Mean
[3]Coefficient of variation (%)
[4]One sample

Table 6.7. Mean concentration of bromide (mg/L) at each sampling depth following second application[1].

Sample Date	Sample Depth (cm) 61	122	183
04/27/87	0.06[2] (32)[3]	0.25 (66)	0.31 (*[4])
04/28/87	2.06 (186)	0.40 (32)	0.11 (*)
04/29/87	6.28 (133)	0.29 (84)	0.56 (*)
04/30/87	7.81 (112)	0.54 (143)	0.95 (93)
05/01/87	7.92 (82)	0.99 (152)	1.47 (127)
05/02/87	5.56 (116)	4.35 (89)	2.02 (114)
05/03/87	5.54 (75)	9.02 (77)	2.96 (112)
05/05/87	3.47 (68)	6.79 (51)	4.62 (100)
05/08/87	1.58 (104)	5.44 (49)	6.97 (128)
05/11/87	1.14 (96)	7.78 (76)	4.99 (82)
05/13/87	0.79 (99)	6.11 (*)	1.91 (56)
05/25/87	0.51 (158)	1.32 (56)	3.04 (113)
06/01/87	0.10 (72)	1.05 (63)	2.20 (130)

[1]Bromide applied 04/27/87
[2]Mean
[3]Coefficient of variation (%)
[4]One sample

application. The maximum concentration of nitrate in these samplers was 5.6 mg/L on 5/03/87. Three samplers located at a depth of 183 cm responded to the application of fertilizer. The maximum concentration of nitrate in these samplers was 8.1 mg/L on 5/08/87. Concentrations of nitrate in the soil solution were not as high as observed concentrations within the groundwater over much of the study site (see Section 6.5.3 for nitrate concentrations in the saturated zone). This is due to the fact that the tractor-mounted broadcast spreader was unable to get close to

the instrumented application area due to the presence of the vacuum and sample tubing and the instrument trailer. As a result, the application rate of fertilizer in this area was reduced. Refer to Appendix B for information on the availability of the data set containing results of all nitrate analyses.

6.5 Chemicals in the Saturated Zone

6.5.1 Bromide

There was no shallow groundwater present on the site between the date of herbicide application (11/12/1986) and Dec. 15, 1986. Bromide was observed in the groundwater on this first well sampling date at a concentration of 0.8 mg/L in well 08-09 (see Figure 4.1 for well locations) which is within the application area. The continued detection of bromide in the groundwater following the first application was sporadic, and the maximum concentration of 3.9 mg/L was detected in well 09-11 on January 12, 1987. The maximum concentration of bromide in the groundwater following the second application (4/27/87) was 5.2 mg/L on May 13th, in well 08-09. Figures 6.18-6.23 show the concentration of bromide within the groundwater over six sampling periods following the first application of bromide. Figures 6.24-6.29 show the concentration of bromide within the groundwater for six sampling periods following the second application of bromide.

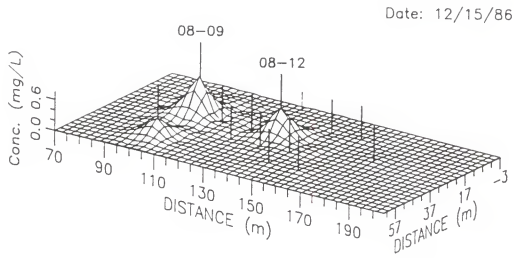


Figure 6.18. Bromide concentration in the groundwater on 12/15/86. Vertical bars indicate sampling locations.

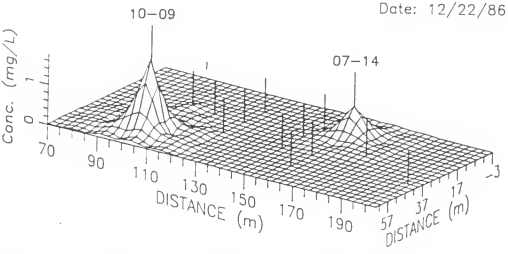


Figure 6.19. Bromide concentration in the groundwater on 12/22/86. Vertical bars indicate sampling locations.

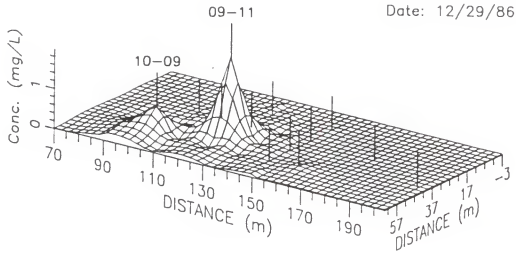


Figure 6.20. Bromide concentration in the groundwater on 12/29/86. Vertical bars indicate sampling locations.

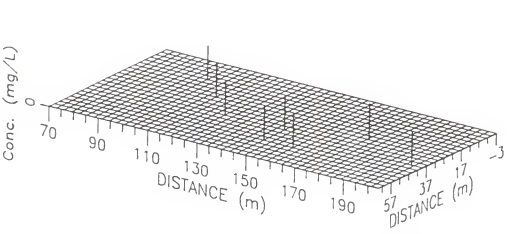


Figure 6.21. Bromide concentration in the groundwater on 1/05/87. Vertical bars indicate sampling locations.

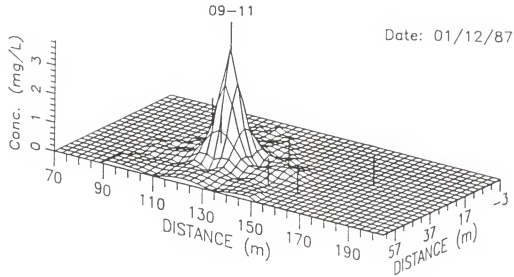


Figure 6.22. Bromide concentration in the groundwater on 1/12/87. Vertical bars indicate sampling locations.

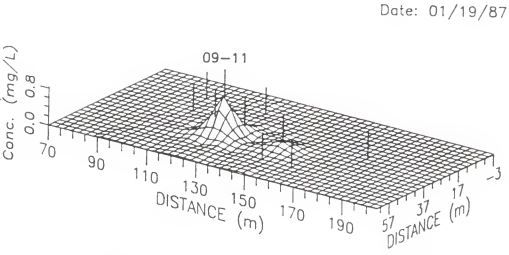


Figure 6.23. Bromide concentration in the groundwater on 1/19/87. Vertical bars indicate sampling locations.

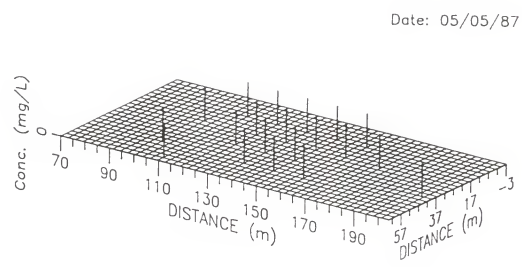


Figure 6.24. Bromide concentration in the groundwater on 5/05/87. Vertical bars indicate sampling locations.

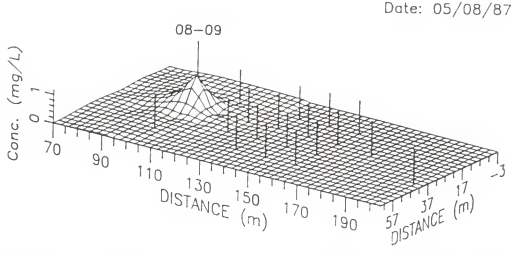


Figure 6.25. Bromide concentration in the groundwater on 5/08/87. Vertical bars indicate sampling locations.

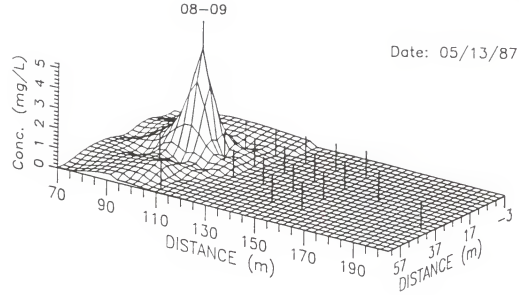


Figure 6.26. Bromide concentration in the groundwater on 5/13/87. Vertical bars indicate sampling locations.

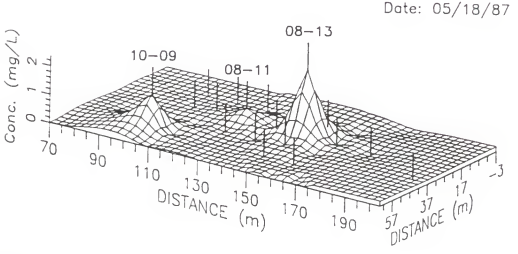


Figure 6.27. Bromide concentration in the groundwater on 5/18/87. Vertical bars indicate sampling locations.

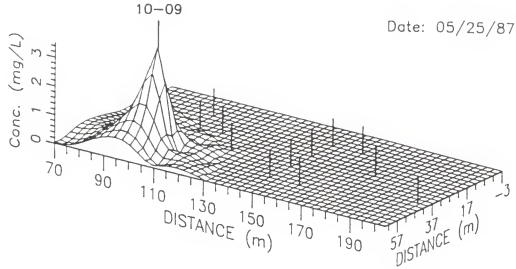


Figure 6.28. Bromide concentration in the groundwater on 5/25/87. Vertical bars indicate sampling locations.

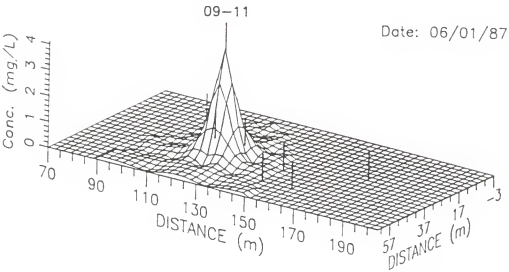


Figure 6.29. Bromide concentration in the groundwater on 6/01/87. Vertical bars indicate sampling locations.

6.5.2 Atrazine

Atrazine first appeared in the groundwater beneath the application area in the samples of Jan. 21. By this date, approximately 45 cm of water had been applied to the site as rainfall and irrigation since application of the herbicides.

Groundwater samples from Jan. 21 through June 6 show what appear to be distinct pulses of atrazine reaching the saturated zone and moving downslope with the saturated flow. These pulses are characterized by low initial concentrations in the groundwater followed by the appearance of atrazine beneath the application area and movement within the groundwater as the water flows downgradient to the west. Figures 6.30 through 6.35 show the concentration of atrazine (in $\mu g/L$) in the groundwater at weekly intervals for a five week period beginning on Feb. 23, 1987. A vertical bar in these figures indicates that a well sample was collected and analyzed from that location. The transport of atrazine with the saturated flow is clearly visible and atrazine moved a distance of approximately 85 m in a period of 21 days.

Figure 6.36 shows the general directions of flow based upon the slope of the water table on May 8, 1987. The slope of the water table on other sampling dates shows that flow would occur in the same general directions. In Figures 6.30 through 6.32 it is observed that atrazine has moved downslope from well 09-11 to 09-14. The average gradient of the water table between these wells during this period was approximately 0.05 m/m. The hydraulic conductivity of the soil was not measured during this study. Assuming a hydraulic conductivity of 14.4 m/day (60 cm/hr) at a depth of approximately 3 m (Carlisle et al., 1978) and an effective

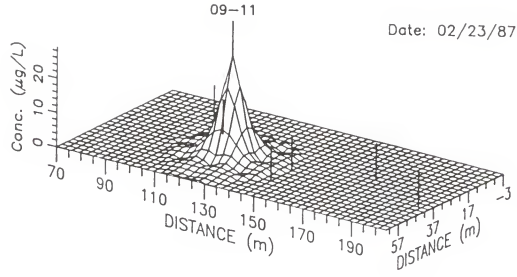


Figure 6.30. Atrazine concentration in the groundwater on 2/23/87. Vertical bars indicate sampling locations.

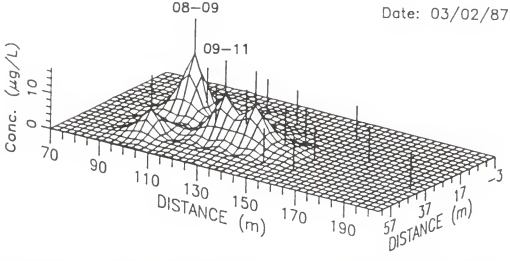


Figure 6.31. Atrazine concentration in the groundwater on 3/02/87. Vertical bars indicate sampling locations.

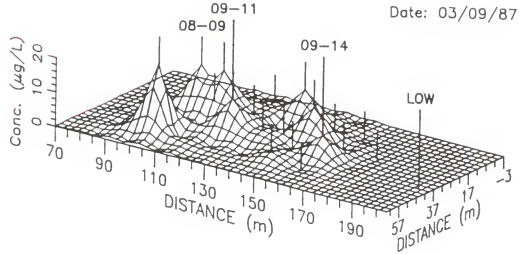


Figure 6.32. Atrazine concentration in the groundwater on 3/09/87. Vertical bars indicate sampling locations.

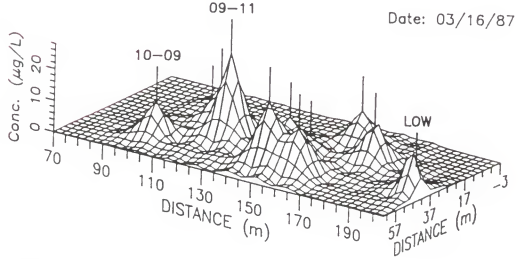


Figure 6.33. Atrazine concentration in the groundwater on 3/16/87. Vertical bars indicate sampling locations.

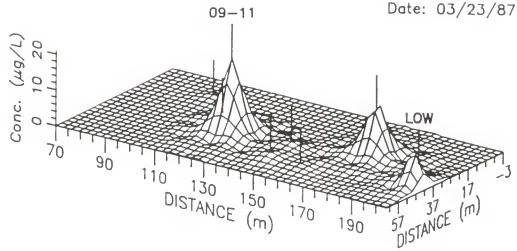


Figure 6.34. Atrazine concentration in the groundwater on 3/23/87. Vertical bars indicate sampling locations.

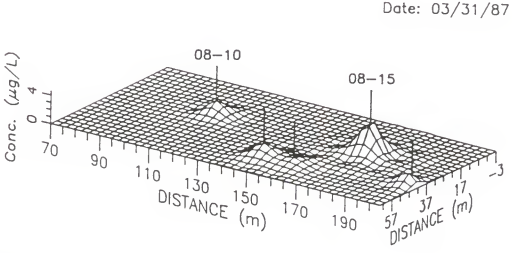


Figure 6.35. Atrazine concentration in the groundwater on 3/31/87. Vertical bars indicate sampling locations.

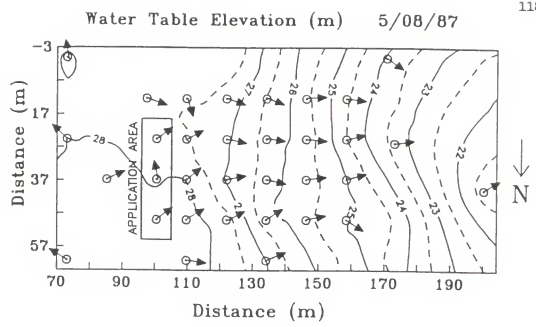


Figure 6.36. Contour plot of water table elevation on 5/08/87 showing direction of flow.

saturated porosity of 0.36 (Table 5.1), it is possible to calculate an estimated water velocity between the wells. The average pore water velocity is calculated as

$$v = k * s / p_e \qquad 6.1$$

where v = average pore water velocity, m/day

k = saturated hydraulic conductivity, m/day

s = hydraulic gradient, m/m

p_e = effective saturated porosity, cm^3/cm^3

Using Equation 6.1 and the values of the variables described above, a pore-water velocity of 2 m/day was calculated. The distance between wells 09-11 and 09-14 is 36 m. Based on the calculated pore-water velocity, water should move the distance between the wells in 18 days. Atrazine was observed to have moved the distance between the wells in 14

days. This would suggest that atrazine was moving faster than the velocity of the water. In Figures 6.32 and 6.33 it is observed that atrazine moved the distance from well 09-14 to well LOW in a period of 7 days. The water table gradient between these wells was approximately 0.7 m/m. The average pore water velocity for the area between these wells was calculated to be approximately 3 m/day. These wells are located a distance of 42 m apart. Based on the calculated water velocity, it should take 14 days for water to move the distance between the wells. Thus, using this method, atrazine would not be expected to have traversed the distance between these wells in 7 days. These simple calculations indicate that the conductivity value is probably too low. It is also possible that atrazine is moving along the top of the restricting layer in large pores or conduits which are not represented by the conductivity value used in the calculations. Without measured values of the saturated conductivity in the saturated zone, it is difficult to explain the rapid movement of atrazine within the groundwater.

Since samples were collected on 7-day intervals and the wells are spaced 12 m apart, there is considerable error associated with estimates of the distance traveled between successive dates and the time required for atrazine to have moved a specific distance. There are also significant errors associated with assuming conductivity values for this site from general soil characterization data. The above examples illustrate that additional site specific data (hydraulic conductivity, effective porosity, etc.) are needed to adequately characterize the observed atrazine transport.

In Figure 6.37, the concentration of atrazine in one well is plotted along with the water table elevation in the well. There appears to be an inverse relationship between concentration and water table elevation or depth of the saturated zone. This well is 20 m downslope from the application area. Based on this figure, it is hypothesized that as the water table rises, the water around the well is primarily coming from percolation through the untreated soil above it which would cause the concentration of atrazine in the vicinity to decrease. During the period that the water table is receding, water which has infiltrated through the application area is flowing past the well, thus increasing the concentration.

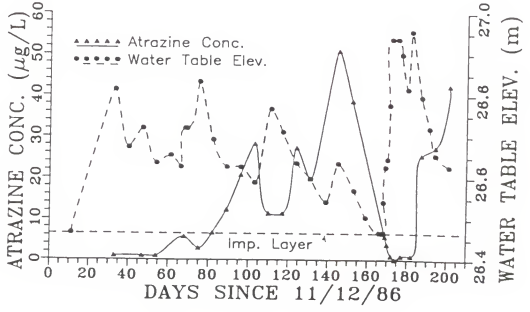


Figure 6.37. Concentration of atrazine and water table elevation in well 09-11.

All concentrations of atrazine in the groundwater were below 0.1 mg/L and in most cases were below 0.01 mg/L. The highest observed concentration was 0.09 mg/L and occurred on 5/5/87 in well 08-09 which is located within the application area. This concentration was observed after the water table had risen due to the application of approximately 24 cm of irrigation water within a period of 8 days. There were high concentrations of atrazine in the groundwater when sampling was discontinued on 6/1/87. Thus, the data collected do not indicate how long atrazine residues persisted on the site. Figures D.1-D.23 in Appendix D show the concentration of atrazine in the groundwater on every sampling date from 1/19/87 through 6/01/87.

6.5.3 Nitrate

Background concentrations of nitrate (as NO_3) in the groundwater were generally below 1 mg/L. Well LOW, which may respond to drainage from other parts of the research farm, often had background concentrations exceeding 15 mg/L. The study site was fertilized on April 16, 1987, and was heavily irrigated beginning on April 27th. The water table on the site started to rise on May 1st. Concentrations of nitrate in the groundwater began increasing on May 3rd. Nitrate concentration levels in the groundwater were observed to be as high as 35 mg/L. Figures 6.38-6.45 show the nitrate concentrations in the groundwater on selected dates.

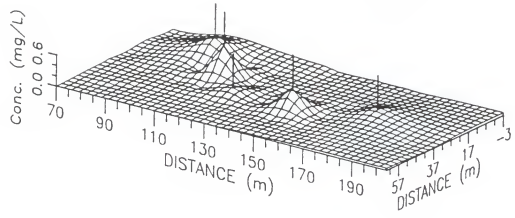


Figure 6.38. Nitrate concentration in the groundwater on 5/01/87. Vertical bars indicate sampling locations.

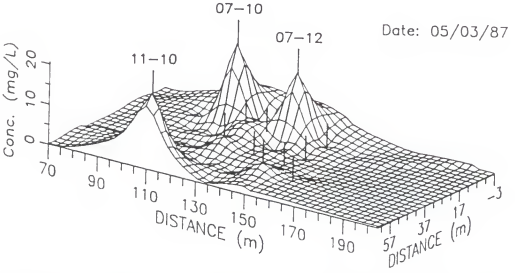


Figure 6.39. Nitrate concentration in the groundwater on 5/03/87. Vertical bars indicate sampling locations.

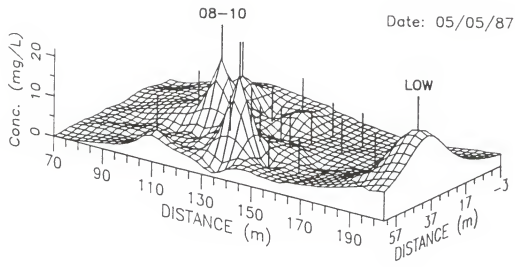


Figure 6.40. Nitrate concentration in the groundwater on 5/05/87. Vertical bars indicate sampling locations.

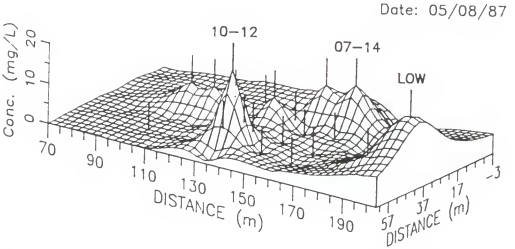


Figure 6.41. Nitrate concentration in the groundwater on 5/08/87. Vertical bars indicate sampling locations.

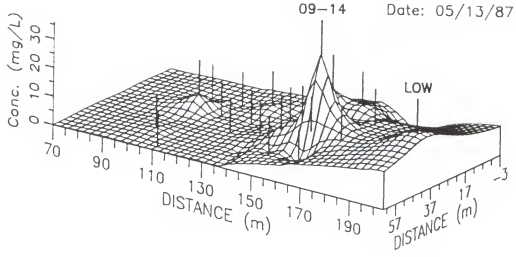


Figure 6.42. Nitrate concentration in the groundwater on 5/13/87. Vertical bars indicate sampling locations.

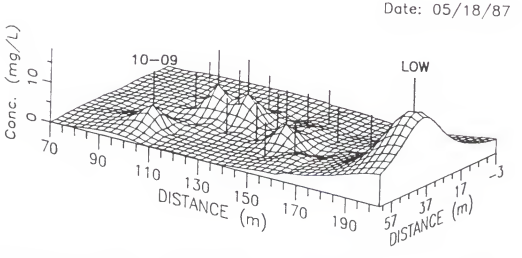


Figure 6.43. Nitrate concentration in the groundwater on 5/18/87. Vertical bars indicate sampling locations.

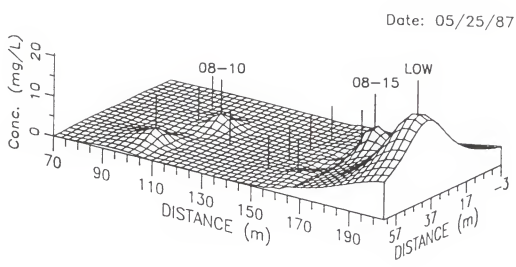


Figure 6.44. Nitrate concentration in the groundwater on 5/25/87. Vertical bars indicate sampling locations.

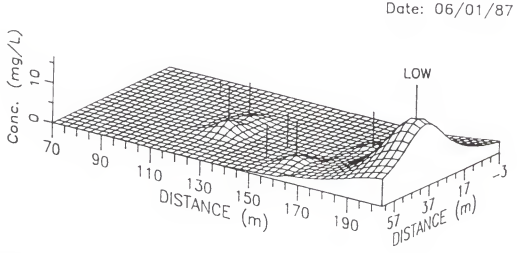


Figure 6.45. Nitrate concentration in the groundwater on 6/01/87. Vertical bars indicate sampling locations.

6.5.4 Chloride

In order to further characterize the flow velocities within the groundwater, 10 L of solution containing 23.8 g/L of chloride (50 g/L of KCl) was poured into well 07-09 on 5/1/87. The chloride was added to the groundwater at a time when nearly continuous percolation was occurring due to irrigation, and the water table was beginning to rise. Chloride concentrations in wells downslope from well 07-09 showed chloride levels exceeding 80 mg/L following the chloride application.

Figures 6.46-6.53 show the chloride concentrations within the saturated zone on selected dates. In Figure 6.46 the background concentration of chloride on May 1, 1987 can be seen to be on the order of 1 mg/L or less. Figure 6.47 shows that chloride from other sources (KCl in the fertilizer) is also entering the groundwater. This is most clearly demonstrated by the high concentration of chloride in well 11-10 which is on the opposite side of the study site from well 07-09 which is where the chloride was introduced into the groundwater. Figures 6.46-6.53 show the general movement of chloride in the groundwater over a period of 29 days.

Discussions presented in Section 6.5.6 will show that additional characterization of soil properties near the restricting layer is needed before the observations of chemical movement within the groundwater can be used to describe flow patterns and velocities within the groundwater. No calculations of flow velocities were performed with the chloride data and no conclusions were drawn from it for presentation here.

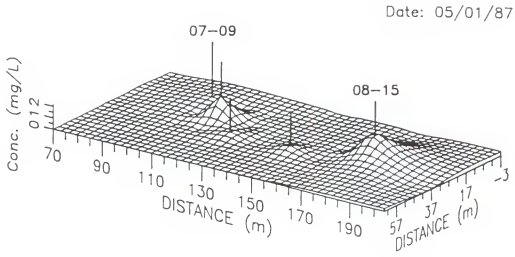


Figure 6.46. Chloride concentration in the groundwater on 5/01/87. Vertical bars indicate sampling locations.

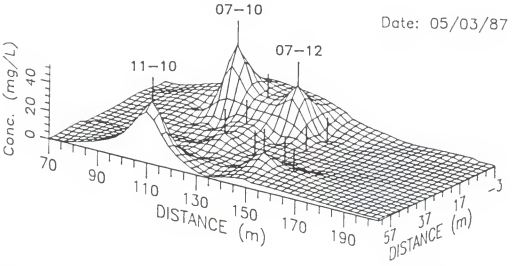


Figure 6.47. Chloride concentration in the groundwater on 5/03/87. Vertical bars indicate sampling locations.

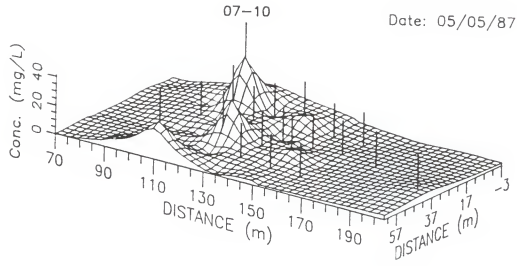


Figure 6.48. Chloride concentration in the groundwater on 5/05/87. Vertical bars indicate sampling locations.

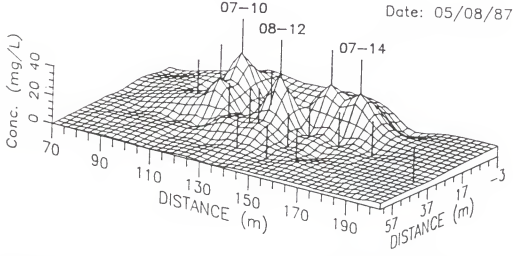


Figure 6.49. Chloride concentration in the groundwater on 5/08/87. Vertical bars indicate sampling locations.

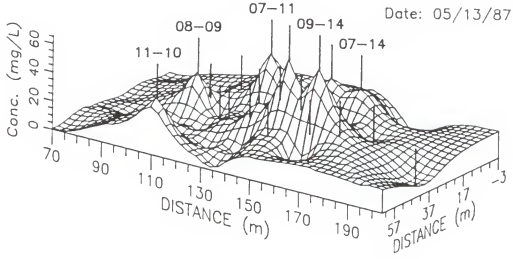


Figure 6.50. Chloride concentration in the groundwater on 5/13/87. Vertical bars indicate sampling locations.

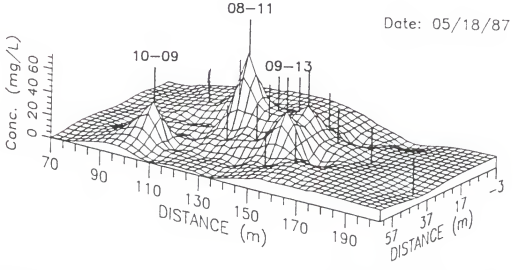


Figure 6.51. Chloride concentration in the groundwater on 5/18/87. Vertical bars indicate sampling locations.

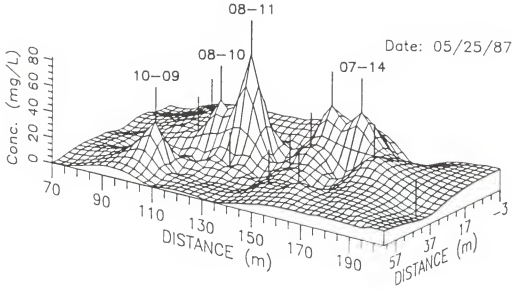


Figure 6.52. Chloride concentration in the groundwater on 5/25/87. Vertical bars indicate sampling locations.

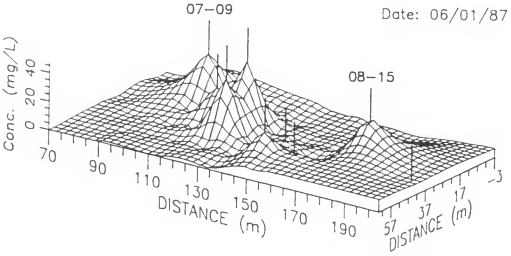


Figure 6.53. Chloride concentration in the groundwater on 6/01/87. Vertical bars indicate sampling locations.

6.5.5 Total mass of chemicals within the saturated zone

In addition to observations of the concentrations of the chemicals within the groundwater, calculations of the total mass of chemicals within the saturated zone were performed. An inverse distance weighting method was used for each observation period to generate a square grid of values over the site. One potential option for gridding data was kriging which has been shown to be more accurate than the inverse distance method (Golden Software, 1987). When kriging was used, however, it was observed that negative concentration values were generated at several intermediate grid points. With the inverse distance method, negative concentrations were not a problem. The data from observation wells spaced 12 m by 12 m apart were gridded to produce data on a 3m by 3m spacing. This was done initially for illustrative purposes.

The data from the wells were gridded in two ways. First, only the wells from which samples were obtained and analyzed were included in the input data set for the gridding process. Second, all wells were included by assigning the concentration in wells without samples a value of zero. The second method was used as an estimate of the minimum mass of a chemical within the saturated zone. The three-dimensional views of the concentrations were judged to better convey to the viewer the values at individual wells when the second method was used as compared to the first method.

Using the concentrations and groundwater depths computed on a 3 m square grid, calculations of water storage and chemical mass storage within the groundwater were performed. These calculations are described in more detail in Section 6.5.6.

The results of these calculations for the two methods of gridding are presented in Table 6.8. Note that the mass of chloride within the groundwater greatly exceeds the amount applied. Significant concentrations of chloride were apparently contributed from other sources such as fertilizer and irrigation water. There are notable differences in the total mass of chemicals stored as calculated from the two methods of gridding the observed data. There is no evidence to suggest that one method is more correct than the other, therefore the values calculated based on the two methods can be considered as the extremes of the possible mass storage in the groundwater with the actual value probably lying somewhere between the extremes. Figure 6.54 shows the mass of atrazine in the saturated zone (based on the second gridding method) during the entire period of observation. What is not shown by Figure 6.54 is the mass of atrazine which may have been transported off-site during the period of observation. In order to estimate the transport of atrazine from the site, it is necessary to first calculate the flux of water from the site. The next section describes the methods used to try to estimate the water and chemical fluxes on the experimental site.

Table 6.8 Total mass of chemicals in the saturated zone

Chemical	Date of Maximum	Maximum Mass in Saturated Zone (g) Method 1[1]	Method 2[1]
Atrazine	5/18/87	8 (5)	4 (3)
Bromide	5/13/87	308 (54)	198 (35)
Nitrate	5/05/87	2916 (23)	1873 (15)
Chloride	5/13/87	16367 (6882)	11812 (4967)

[1]Method 1: using only measured values in gridding procedure
Method 2: assuming that wells without observations had a concentration of zero
[2]Numbers in () are percent of total application

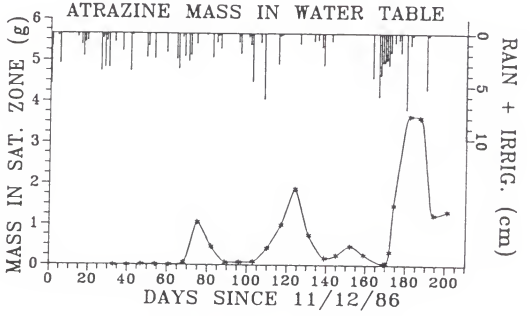


Figure 6.54. Total mass of atrazine stored in the saturated zone. Atrazine was applied to the site on 11/12/86.

6.5.6 Water Balance Calculations

An attempt was made to calculate a water and chemical budget for the study site. The primary objective of this exercise was to calculate the mass flux of chemicals moving off the site. The mass of a chemical stored in the saturated zone at the end of the monitoring period plus the mass of chemical transported off-site should be comparable to the total mass of chemical leached from the root zone as predicted by the models.

6.5.6.1 Nodes and subareas

As noted in section 6.5.5, the data for water table elevation, restricting layer elevation, and chemical concentrations were gridded on a 3 m by 3 m spacing. Each grid point was considered to be a node for the calculations described below. The study area was divided into six subareas as shown in Figure 6.55. The subareas were numbered from the top of the slope. The chemical application area was entirely contained within subarea number 2 as shown in Figure 6.55.

6.5.6.2 Nodal calculations

The slope of the water table in both the x and y directions was calculated at every node within the site using centered-difference techniques, ie. along the y-axis the slope at node j is calculated as:

$$\text{slope}(j) = [\text{elev}(j-1) - \text{elev}(j+1)] \,/\, [2 * \delta y] \qquad 6.1$$

where slope(j) = slope of the water table in m/m, elev(j-1) and elev(j+1) = elevation of the water table at nodes j-1 and j+1, respectively, in m, and δy is the spacing between nodes in m. The gradient of the water

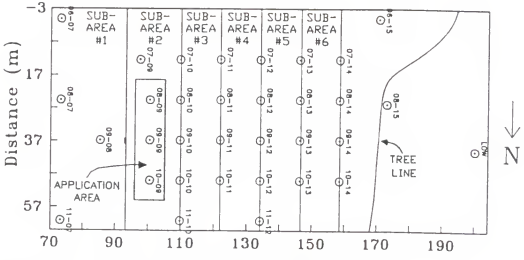


Figure 6.55. Subareas used in water balance calculations.

table, as used in flux calculations, is the negative of the slope defined above. The flux of the water at any node was calculated as:

$$flux(j) = -cond(j) * slope(j) \qquad 6.2$$

where flux(j) = the water flux at node j in m/day, cond(j) = the saturated conductivity at node j in m/day, and slope(j) is as defined above. The volumetric flowrate of water through the area represented by node j was calculated as

$$Q(j) = flux(j) * wtd(j) * \delta y \qquad 6.3$$

where Q(j) = volumetric flowrate past node j in m^3/day, wtd(j) = groundwater depth at node j in m, and flux(j) and δy are as defined above. The mass of chemical moving past a node was calculated as the product of the volumetric flowrate, Q, and the solution concentration of the chemical at that node.

To compute the change in water storage between sampling periods, it was necessary to calculate the relationship between drained volume and

water table depth. The slope of the drained volume-water table depth relationship is called the drainable porosity. A program called DVOLWTD was used to calculate the drainable porosity. The DVOLWTD program is provided with the water table management model DRAINMOD (Skaggs, 1978). The program uses the soil-water characteristic data for the profile and computes the volume of water drained as the water table falls. The soil water characteristic data input to DVOLWTD was obtained from Hook (1985). Graphs of the drained volume-water table depth relationship and the soil-water characteristic curve are presented in Figures C.3 and C.4 in Appendix C. The drained volume was calculated at every node based upon the depth to the water table at that node.

The mass of chemical stored (sorbed and in solution) in the volume represented by each node was calculated based upon the groundwater depth at the node, the concentration of the chemical in solution, and the partitioning coefficient for the chemical. The K_{OC} for atrazine used in this study is 163 cm^3/g (Table 5.2). The organic carbon content of the soil above the restricting layer was assumed to be 0.03% (Table 5.1). Thus the K_D for atrazine in the lower soil zones is 0.049. The drained volume and chemical storage values calculated as described above were summed over each subarea.

6.5.6.2 Boundary and subarea flux calculations

The total volumetric flowrate of water was calculated for each boundary in a subarea. This was done by summing the flowrates calculated above for all the nodes along a boundary. The sum of the flowrates calculated for the four boundaries yields the net flowrate into or out of

the subarea on that date. The calculations described above were performed for all nodes and subareas for the 28 sampling dates in this study.

6.5.6.3 Mass balances between observation dates

The net flowrate between sampling dates for each subarea was calculated by averaging the net flowrates calculated on the two dates. The average net flowrate multiplied by the interval between the sampling dates resulted in an estimate of the total volume of water which had moved into or out of a subarea by saturated flow between the dates. The percolation volume during the interval between dates predicted by PRZM was used to calculate the volume of water added to each subarea due to rainfall or irrigation. The sum of the volume of water added or removed from a subarea by saturated flow and the volume added by percolation gave an estimate of the predicted change in water volume in the subarea between the sampling dates.

The change in drained volume in a subarea between sampling dates was assumed to represent the actual change in water volume in that subarea. Thus, the predicted change in water volume could be compared to a "measured" value.

Mass balances of chemicals within the saturated zone were done in a similar manner. Chemicals were assumed to be added to the saturated zone only in subarea number 2 which contained the application area. The mass of chemical leaching past the bottom of the soil profile (2.62 m) predicted by PRZM was multiplied by the area of the application area to calculate the total mass of chemical added to subarea number 2.

Prediction of mass transport across boundaries was performed as described above for water. The mass storage of chemical calculated for each subarea was compared to the predicted storage based on mass inflows and outflows to a subarea.

6.5.6.4 Results

The conductivity of the soil in the saturated zone was not measured. As an initial estimate, a conductivity of 14.4 m/day (60 cm/hr) was used (Carlisle et al., 1978). For periods when the water table was falling and no percolation was added, the predicted and observed change in water storage on 4 of the subareas agreed reasonably well. Subareas 3 and 6, however, would accumulate water when such accumulation was not observed. In order to avoid accumulation of water within subareas 4 and 6, a conductivity value on the order of 40 m/day was required along the boundary between subareas 4 and 5, and the boundary at the bottom (western edge) of area 6. This would suggest that the cross-sectional area of flow across these boundaries was not adequately characterized.

With the higher conductivity values at the boundaries described above, the predicted and observed changes in water balances for the site were in reasonable agreement when no percolation was added. When percolation was predicted during the interval between sampling dates, however, the mass balances were not acceptable. The calculated change in storage in a subarea suggested that water accumulated within the subarea when measurements indicated that there was a net loss of water in that area. Whenever percolation was added, the predicted change in

storage would nearly always be substantially (order of magnitude) higher than the observed change.

There are a number of possible reasons why the mass balances of water did not agree. One reason is that both PRZM and GLEAMS assume that all percolation through the soil profile occurs within one day. The actual movement of percolating water through the profile may be much slower than this and thus, may be sustained over significantly longer periods. Therefore, water which was predicted to have been added to the profile during the interval between sampling dates may actually have slowly entered the groundwater over several sampling intervals. It is possible that PRZM was overestimating the volume of percolation. GLEAMS, however, predicted nearly identical percolation volumes using an entirely different calculation procedure. This would suggest that the predicted percolation volumes are reasonable.

Another source of error may be the assumption that the conductivity is constant over the depth of the groundwater. The conductivity may increase as the groundwater depth increases. There may also be large pores or conduits near the restricting layer which can move water much more rapidly than would be predicted using the methods described above. There is also significant error associated with the actual location of the restricting layer. The bottom of the wells were assumed to be placed on top of this layer. During placement of the wells, the augered holes did not stop exactly on top of the restricting layer. The auger had to cut into the restricting layer in order visually determine (due to color and texture change) that the restricting layer had been reached. There could easily be variations in the depth of penetration in the restricting

layer of 5 cm. Since the depth of flow on this site was often less than 10 cm, an error of +/- 5 cm in the location of the restricting layer would significantly affect the calculated depth of flow. As noted above, the restricting layer was determined by visual observation of color and texture changes. The depth at which the vertical hydraulic conductivity of this layer becomes small enough to cause saturation may not correspond to the visually determined top of the layer. There may also be some small channels on the surface of the restricting layer in which significant flow could occur that are not shown by the wells. This is demonstrated by the fact that conductivities along the two boundaries mentioned above had to be increased significantly above the values used elsewhere in order to move sufficient quantities of water across those boundaries. The potential water movement into the restricting layer was also not accounted for.

There is much additional work to be done before an adequate water balance can be performed on this site. Additional characterization of soil properties in the saturated zone and improved estimates of the location of the restricting layer are needed.

Since the water balance attempts were generally unsuccessful, chemical balances, although calculated, were not considered further.

Two FORTRAN programs were written to perform the calculation described in the previous section. Program ANALYZE performs nodal and boundary flux calculations for each observation date and is presented in Figure C.1 in Appendix C along with a sample output (Table C.1). Program FLUX computes the water and chemical balances between sampling periods

and is presented in Figure C.2 in Appendix C along with a sample output (Table C.2).

6.5.7 Summary of observations of chemical transport

The discussion of the observed concentrations of atrazine and the tracers has been descriptive in nature. This is due to the fact that additional data are required in order to quantitatively assess the results.

Each of the applied chemicals (except for alachlor) was observed to move through the soil profile and enter the groundwater. However, insufficient data were collected from which the quantity or velocity of water percolating through the soil profile could be directly determined. Similarly, movement of chemicals within the groundwater was observed. There were insufficient data, however, to quantitatively assess the volume and velocity of flow within the saturated zone to acceptable levels. The tracer data were inconclusive due to the transient nature of the groundwater. Some of the wells would dry rapidly. The wells along the boundary between subareas 4 and 5 (Figure 55) would often be dry when wells on both sides of this boundary would have water in them. This would indicate that some saturated flow was occurring across this boundary in small channels in the restricting layer which did not coincide with the established well network ie. the wells did not intercept these channels.

6.6 Model Results and Comparisons

The PRZM and GLEAMS models were run to simulate the time period from 1/1/86 through 12/31/87. Simulation of the system for the ten months in 1986 prior to application was done to minimize the effects of initial conditions. The simulated total mass flux of pesticides, bromide, and nitrates below the root zone during the sampling period are shown in Table 6.9. The mass flux of the chemicals to the bottom of the profile as simulated by PRZM is also included in Table 6.9. The models predicted that no additional movement of the applied chemicals below the root zone occurred after 6/1/87.

Table 6.9 Simulated mass flux of chemicals.

Chemical	Simulated Mass Flux (g/ha)		
	GLEAMS[1]	PRZM[1]	PRZM[2]
Atrazine[4]	2970 (60.6)[3]	2314 (47.2)	1154 (23.6)
Alachlor[5]	516 (10.5)	165 (3.4)	10 (0.2)
Bromide[6]	23604 (87.4)	23718 (87.8)	17116 (63.4)
Nitrate[6]	10657 (57.3)	14551 (78.23)	9376 (50.4)

[1]Bottom of root zone
[2]Bottom of profile
[3]Percent of application
[4]Plant uptake coef. = 0.65
[5]Plant uptake coef. = 0.52
[6]Plant uptake coef. = 1.00

GLEAMS predicted a higher percentage of herbicide leaching than did PRZM. One reason for the difference may be that GLEAMS defines 6 major soil layers (there is a 1 cm layer at the soil surface) and thus averages

soil properties such as the organic carbon content over larger depths relative to the smaller layers utilized by PRZM. The increased number of layers in PRZM allows the calculated layer properties to more nearly match the profile description input into the model. Another reason for the differences in model predictions may be the method by which pesticide transport is calculated in each model. In PRZM, a form of the advection-dispersion equation is solved (after water velocities have been determined separately) using finite-difference techniques to calculate pesticide transport. In GLEAMS, pesticide transport is calculated by sequentially moving the chemicals between layers based on water flux and the concentration of the chemical in each layer. After the chemicals have been added to or removed from a layer, the mass of the chemical is redistributed between the sorbed and solution phases based upon the partition coefficient in that layer.

The predicted leaching of bromide by the two models was similar. Closer examination indicates that GLEAMS predicted higher fluxes of bromide for the first application, and PRZM predicted higher fluxes for the second application. The overall effect was to predict nearly identical bromide fluxes. The nitrate leaching predicted by PRZM was higher than the GLEAMS prediction due to PRZM's higher predicted percolation volumes after the nitrate was applied as shown in Figure 6.56. Overall, the percolation predicted by the models is very similar. A small adjustment in the leaf area index (LAI) in GLEAMS could result in closer agreement between the percolation predicted by the models.

Figures 6.57-6.62 show the measured concentrations of atrazine in the soil profile and the corresponding predictions by PRZM. Figures

6.63-6.68 present similar data for alachlor. Results from GLEAMS are not included in these figures due to the fact that GLEAMS only outputs results for days on which there was sufficient rainfall to cause percolation beneath the root zone. There were no GLEAMS results available for most of the days shown in Figures 6.57-6.68. The results in Figures 6.57-6.62 suggest that the selected partition coefficient, K_{ow}, for atrazine may be too low. The model appears to predict that atrazine would leach more rapidly than the observed rate of movement. It also appears that atrazine is persistent in the soil and that the 78 day half-life used as a model input may also be too low. Figures 6.63-6.68 clearly show that the half-life selected for alachlor was too low. It is difficult to assess the influence of the K_{ow} used for alachlor since the low half-life degraded the alachlor so rapidly that very little was available to be leached.

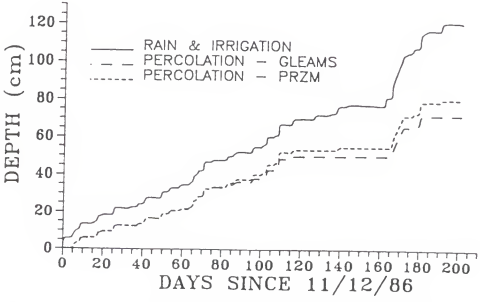


Figure 6.56. Comparison of percolation volumes predicted by GLEAMS and PRZM.

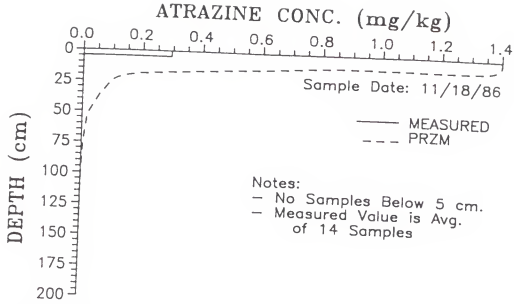


Figure 6.57. Comparison of measured and PRZM predicted atrazine concentrations in the soil on 11/18/86.

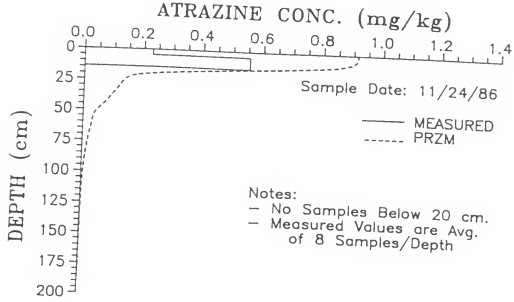


Figure 6.58. Comparison of measured and PRZM predicted atrazine concentrations in the soil on 11/24/86.

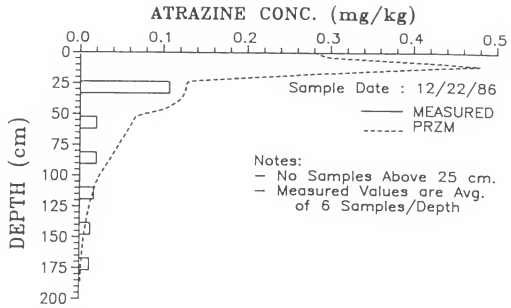


Figure 6.59. Comparison of measured and PRZM predicted atrazine concentrations in the soil on 12/22/86.

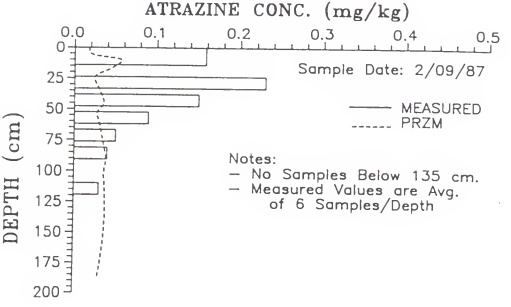


Figure 6.60. Comparison of measured and PRZM predicted atrazine concentrations in the soil on 02/09/87.

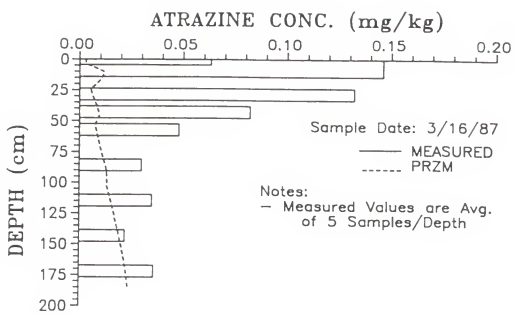


Figure 6.61. Comparison of measured and PRZM predicted atrazine concentrations in the soil on 03/16/87.

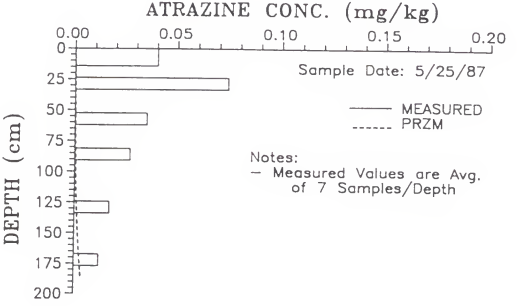


Figure 6.62. Comparison of measured and PRZM predicted atrazine concentrations in the soil on 05/25/87.

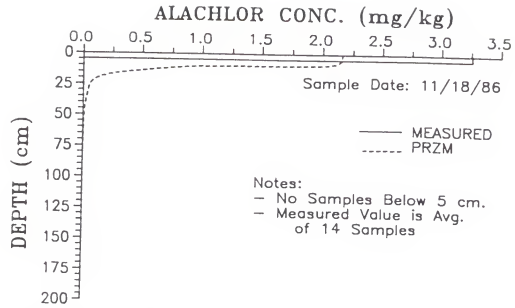


Figure 6.63. Comparison of measured and PRZM predicted alachlor concentrations in the soil on 11/18/86.

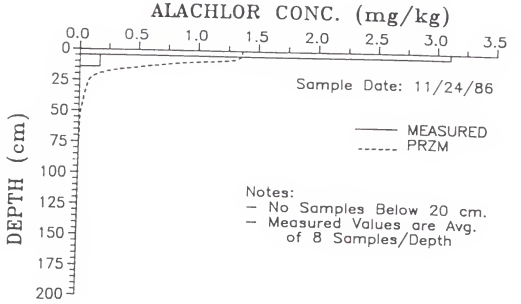


Figure 6.64. Comparison of measured and PRZM predicted alachlor concentrations in the soil on 11/24/86.

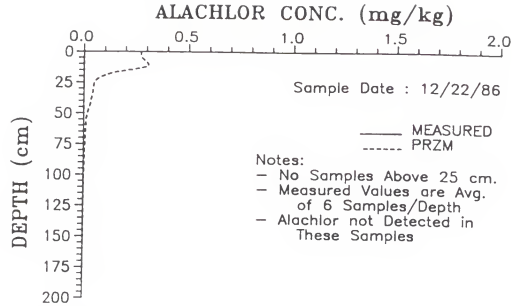


Figure 6.65. Comparison of measured and PRZM predicted alachlor concentrations in the soil on 12/22/86.

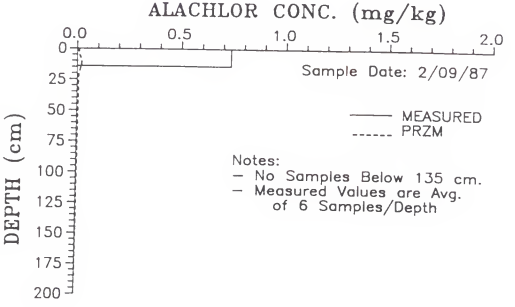


Figure 6.66. Comparison of measured and PRZM predicted alachlor concentrations in the soil on 02/09/87.

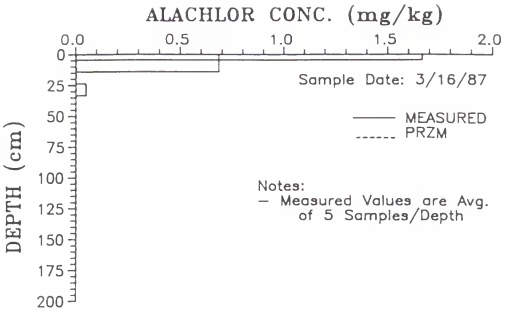


Figure 6.67. Comparison of measured and PRZM predicted alachlor concentrations in the soil on 03/16/87.

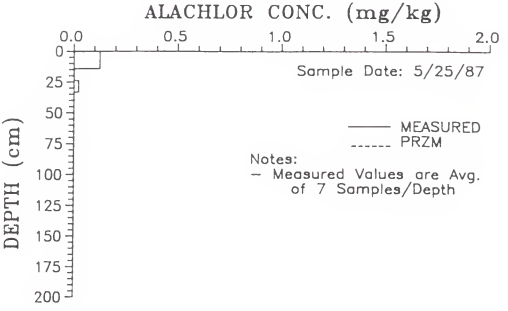


Figure 6.68. Comparison of measured and PRZM predicted alachlor concentrations in the soil on 05/25/87.

Figures 6.69-6.71 show the measured and predicted concentrations of bromide in the soil solution at depths of 61, 122, and 183 cm following the first application of bromide. Figures 6.72-6.74 show the bromide concentrations at the same depths following the second bromide application. PRZM predicted concentrations are shown for both free drainage and restricted drainage options (see Section 5.2.3 for discussion of drainage options in PRZM). In almost every case shown in Figures 6.69-6.74, the time to peak concentration of the measured data falls between the predicted time to peak concentration for the two drainage options. Thus it would appear that a drainage rate parameter could be selected which would match the measured time to peak concentration more closely. This would be part of a calibration procedure. Calibration of the models was not attempted since there is only one year of data from this study and if this data is used for calibration, there would be no independent data to test the calibrated models against.

It should also be noted in Figures 6.69-6.74 that in all cases the measured and predicted peak concentrations agreed to within an order of magnitude, and that in most cases they agreed to within a factor of 2 to 3. Thus for the case of the bromide applications, PRZM would meet the criteria for acceptance suggested by Hedden (1986). In the work presented here PRZM and GLEAMS were essentially run in a screening mode. Many of the model parameters were selected from tables and other information contained the model's users manuals. Parameters were not optimized or calibrated to produce the best fit. At this stage of data collection and model use, it was decided to investigate how the models

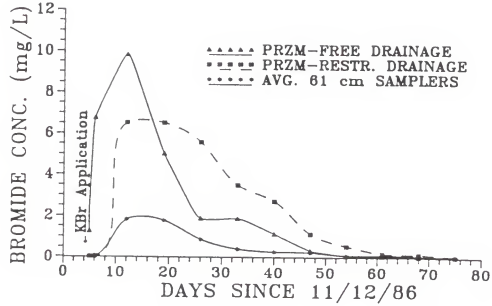


Figure 6.69. Measured and PRZM predicted bromide concentrations in the soil solution at a 61 cm depth following the first application.

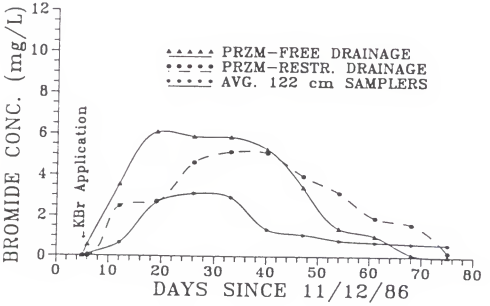


Figure 6.70. Measured and PRZM predicted bromide concentrations in the soil solution at a 122 cm depth following the first application.

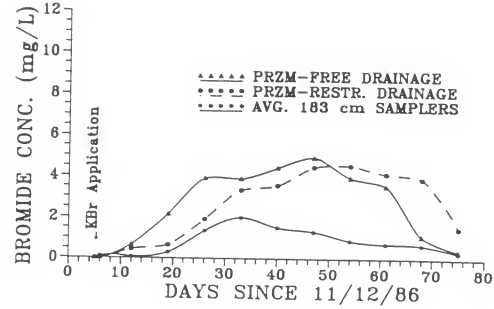


Figure 6.71. Measured and PRZM predicted bromide concentrations in the soil solution at a 183 cm depth following the first application.

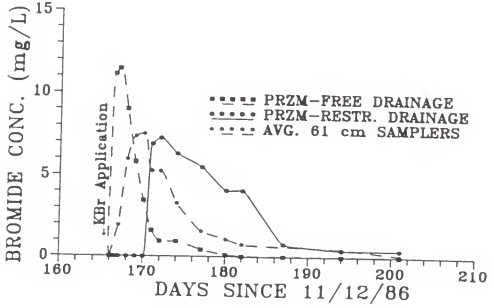


Figure 6.72. Measured and PRZM predicted bromide concentrations in the soil solution at a 61 cm depth following the second application.

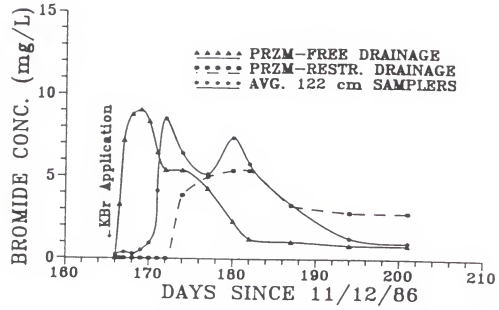


Figure 6.73. Measured and PRZM predicted bromide concentrations in the soil solution at a 122 cm depth following the second application.

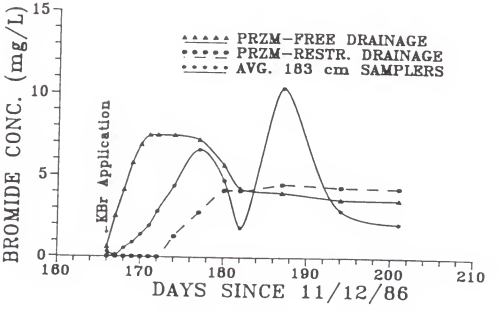


Figure 6.74. Measured and PRZM predicted bromide concentrations in the soil solution at a 183 cm depth following the second application.

would perform when run with minimal site-specific inputs. A governmental regulator would certainly not have detailed site specific data available for all the combinations of crop/soil/chemical that may be of interest. Such a user would be unlikely to have site measured application rates for use as input. If the normal application rates for atrazine and alachlor are 4.9 kg/ha on the cropping system which is being simulated, the model user would certainly use those values as the input to the model. They would not know that the actual average application rates may only be 3.4 kg/ha.

A small number of soil solution samples from samplers were extracted for analysis of atrazine residues. The volume of these samples was between 30 and 40 mL. Figure 6.35 shows the measured and PRZM simulated concentrations of atrazine in the soil solution at a depth of 61 cm. PRZM was run in the free drainage mode using the calculated plant uptake coefficient of 0.65.

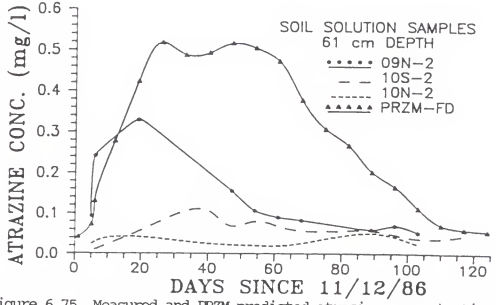


Figure 6.75. Measured and PRZM predicted atrazine concentrations in the soil-water at a depth of 61 cm.

The maximum observed concentration of atrazine at the 61 cm depth was approximately 0.35 mg/L and the maximum concentration predicted by PRZM was 0.57 mg/L. The predicted and observed maximum concentrations are again within a factor of 2. The 0.35 mg/l maximum observed value however was from one of three samplers from which some samples were extracted. The data from the other two samplers do not show any distinct peak concentration, however, the concentrations are within an order of magnitude of the predicted values. The models were run with the intended application rate of 4.9 kg/ha, but the actual application samples suggest the true application rate was 3.4 kg/ha. The time to peak concentration between predicted and observed was reasonably close; however PRZM simulated a much broader peak than was observed.

The simulated transport of applied chemicals by the two models were in reasonable agreement with each other. The differences are probably due to the detail of discretization of the root zone and the method of calculated chemical transport as discussed previously. PRZM can more nearly match the observed soil layering than can GLEAMS due to the fact that GLEAMS describes the entire root zone with only seven layers. PRZM and GLEAMS both simulated large losses of atrazine from the root zone (40 and 62% of application, respectively). The PRZM simulated transport of atrazine to a depth of 2.6 m amounted to 24% of the mass applied. As discussed previously, less than 4% of the applied atrazine could be accounted for on a given day within the saturated zone. This figure does not account for storage in the vadose zone or mass transported off site.

CHAPTER 7
SUMMARY AND CONCLUSIONS

A field experiment was conducted to observe the movement of two surface applied herbicides (atrazine and alachlor) through the soil profile and within a shallow water table aquifer. Bromide was applied to the soil surface to act as a non-adsorbed tracer of water movement. The nitrate component of a surface applied fertilizer was also monitored through the soil profile and within the water table.

Instrumentation was installed on a 0.7 ha field for collection of soil water samples from the unsaturated zone and water samples from the saturated zone. Soil water samples were collected with soil solution samplers installed in six groups of three samplers each at depths of 61, 122, and 183 cm. Shallow groundwater samples were collected from 5 cm diameter PVC monitoring wells. The wells were installed on a 12 by 12 m grid over the study site. Soil samples were collected several times during the study from various depths beneath the application area.

Methods were developed to extract the herbicide residues from soil and water samples. Herbicide residue samples were analyzed on a gas chromatograph using a nitrogen-phosphorus detector. Concentrations of the inorganic tracers were analyzed using an ion chromatograph.

The uniformities of application of atrazine, alachlor, and bromide were measured. There was considerable variability observed in the application rates (kg/ha) of the three chemicals. The chemicals were

applied using a boom sprayer developed for use in chemigation research. The results indicate that chemical application rates from conventional farm equipment are likely to be highly variable. The variability of application, in addition to the variability of soil properties, makes prediction of field measured concentrations difficult.

Concentrations of bromide and nitrate at all three monitored depths showed a high degree of variability. The peak concentration and the time required to reach the peak concentration varied significantly between sampling locations. The effect of this variability may be to reduce maximum concentrations and increase the duration of loading reaching a water table.

Atrazine moved rapidly through the sandy soil on the study site. Concentrations of atrazine in the soil water at a depth of 61 cm reached 0.35 mg/L 19 days after application. Detectable levels of atrazine reached the water table 2 months after application. Atrazine concentrations as high as 0.09 mg/L were observed in the groundwater nearly 6 months after application.

Alachlor was not detected in the soil below a depth of 45 cm. No trace of alachlor was detected in the groundwater samples.

As much as 20 percent of the nitrate from the fertilization of the study site was observed to be in the groundwater on a given date. The decreasing concentrations of nitrate in the groundwater with continued percolation of water suggests that most of the nitrate was leached from the soil profile.

The PRZM and GLEAMS models were found to be easy to use. Sufficient information is provided in the user manuals for estimation of required

parameters. When the models were run using pesticide properties obtained from the manuals, simulated leaching and degradation of the herbicides exceeded field observations. The models were not calibrated to the observed data.

The data collected during this study provide a picture of the concentrations of various chemicals within the soil profile and groundwater on specific dates. Data to accurately quantify the movement of water on the site, however, are missing. The models predict the mass flux of chemicals past a given point (usually the bottom of the root zone). The observed data from this first year study are insufficient to determine mass fluxes and therefore can not be used to adequately test the mass flux predictions of the models. PRZM simulation results were used to compare observed and predicted concentrations of the chemicals. This is because PRZM will report the simulated concentrations at any depth on a daily basis. GLEAMS will only output soil concentration data ($\mu g/g$) on days with a storm event that causes leaching below the root zone. This makes it difficult to compare GLEAMS predictions with samples taken between storm events.

The results presented in this dissertation represent data from the first year of a field study and application of two pesticide transport models to the conditions present at the field site during the study. Much has been learned about sample collection, sample analysis, and the limitations of the data which have been collected, for both describing the movement of the chemicals and testing model predictions.

CHAPTER 8
RECOMMENDATIONS FOR IMPROVEMENTS AND FURTHER STUDY

Additional information must be collected in order to quantify the mass flux of chemicals and water within the vadose zone and the groundwater.

The water content, or tension, of the soil must be observed on a more frequent basis. Soil moisture blocks or tensiometers with pressure transducers could be read on frequent intervals (5 min - 1 hr) using a datalogger. If there is sufficient sensitivity to the small changes in water content on this soil (0.13 - 0.02 cm^3/cm^3) then the total flux of water moving by the tensiometers could be estimated.

Further characterization of the restricting layer is needed. Core samples should be taken from throughout the soil profile and presumed restricting layer. Measurements of hydraulic conductivity, bulk density, particle size distribution, and organic matter content should be made on the cores. These data would refine estimates of soil properties throughout the soil profile and further define the location of the restricting layer. A detailed mapping of the surface of the restricting layer using ground penetrating radar (GPR) would help to define the locations and extent of small channels or irregularities.

Knowing where the bottoms of the observation wells are located relative to the restricting layer will improve the estimates of flow depth. Improved values for conductivity and the cross-sectional area of

flow at a location will improve calculations of water flux. An estimate of the seepage of water through the restricting layer may also improve the water budget for this site. The current system adequately defines the elevation of the water table surface from which gradients are calculated.

Model validation will require (in addition to the soil properties listed above) that the partition coefficient and degradation rate for the chemical of interest be measured from on-site soil samples. The accuracy of model predictions of mass fluxes should improve significantly by using site-specific data. Careful measurement of application rates should be made. Measured application rates were lower than the intended rates. The models should also be tested using the observed range of sensitive soil and chemical parameters.

A second year study on this same site should be done to try to quantify some of the characteristics or properties described above. In addition, the study should monitor the movement of atrazine, one other pesticide, bromide, and nitrate. The usefulness of the second year data would reflect and be enhanced by the lessons learned from the work done to complete this dissertation.

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APPENDIX A

MONITORING WELL STATISTICS

Table A.1 Monitoring Well Statistics

WELL / STATION	INSTALLED BY	DATE INSTALLED	DISTANCE FROM RISER 6-1 [METERS][1]		CASING LENGTH	ELEVATION (METERS)[2]		
			X	Y	[METERS]	TOP OF CASING	SOIL SURFACE	RESTR. LAYER
06-07	USDA	2/7/85	0.00	73.15	3.14	30.85	30.42	27.71
08-07	USDA	2/7/85	24.38	73.15	2.84	30.84	30.40	28.00
11-07	USDA	2/7/85	60.96	73.15	2.59	30.70	30.24	28.11
09-08	UF	3/23/87	36.58	85.34	2.91	30.93	30.41	28.02
07-09	USDA	2/7/85	12.19	97.54	3.58	30.86	30.30	27.28
08-09	UF	5/22/86	24.38	100.58	3.40	30.76	30.26	27.36
09-09	UF	5/22/86	36.58	100.58	2.83	30.76	30.25	27.93
10-09	UF	5/22/86	48.77	100.58	3.17	30.75	30.22	27.58
07-10	UF	5/22/86	12.19	109.73	3.18	30.64	30.13	27.46
08-10	USDA	2/7/85	24.38	109.73	3.83	30.56	30.04	26.73
09-10	UF	5/22/86	36.58	109.73	2.53	30.52	30.03	27.99
10-10	UF	5/22/86	48.77	109.73	2.45	30.56	30.02	28.11
11-10	USDA	2/7/85	60.96	109.73	2.47	30.64	30.13	28.17
06-11	UF	3/11/88	0.00	121.92	3.07	30.69	30.08	27.62
07-11	USDA	2/7/85	12.19	121.92	3.26	30.29	29.74	27.03
08-11	UF	5/21/86	24.38	121.92	3.34	30.16	29.64	26.82
09-11	UF	5/21/86	36.58	121.92	3.62	30.09	29.55	26.47
10-11	UF	5/21/86	48.77	121.92	2.68	30.09	29.57	27.41
07-12	UF	5/21/86	12.19	134.11	3.56	29.77	29.28	26.21
08-12	USDA	2/7/85	24.38	134.11	3.60	29.57	29.09	25.97
09-12	UF	5/21/86	36.58	134.11	3.66	29.54	29.02	25.88
10-12	USDA	2/7/85	48.77	134.11	3.38	29.53	29.07	26.15
11-12	USDA	2/7/85	60.96	134.11	2.67	29.68	29.19	27.01
07-13	USDA	2/7/85	12.19	146.30	3.88	29.21	28.70	25.33
08-13	UF	5/21/86	24.38	146.30	3.67	29.05	28.51	25.38
DEEP	UF	11/10/86	30.48	146.30	10.25	28.92	28.46	18.67[3]
09-13	UF	5/21/86	36.58	146.30	3.93	28.93	28.42	25.00
10-13	UF	5/21/86	48.77	146.30	3.80	28.86	28.43	25.06

Table A.1 Continued.

WELL / STATION	INSTALLED BY	DATE INSTALLED	DISTANCE FROM RISER 6-1 [METERS][1] X	Y	CASING LENGTH [METERS]	ELEVATION (METERS)[2] TOP OF CASING	SOIL SURFACE	RESTR. LAYER
07-14	UF	5/20/86	12.19	158.50	4.45	28.62	28.09	24.17
08-14	UF	5/20/86	24.38	158.50	4.01	28.35	27.85	24.34
09-14	UF	5/20/86	36.58	158.50	3.22	28.11	27.63	24.89
10-14	USDA	2/7/85	48.77	158.50	3.54	27.97	27.55	24.43
06-15	USDA	2/7/85	0.00	170.69	4.18	28.14	27.72	23.96
08-15	USDA	2/7/85	25.15	172.83	4.86	27.31	26.85	22.45
LOW	USDA	2/7/85	39.62	200.18	1.67	22.38	22.11	20.71

1 ORIGIN @ SPRINKLER RISER 6-1 WITH X POSITIVE TO NORTH AND Y POSITIVE TO WEST
2 ELEVATION OF TOP OF SPRINKLER RISER 09-09 SET EQUAL TO 30.48 METERS
3 ELEVATION OF BOTTOM OF WELL

APPENDIX B

HOW TO GET COMPLETE DATA SET

Complete data sets showing the concentrations of all chemicals in both water and soil samples can be obtained by writing to:

Matt C. Smith
Agricultural Engineering Department
University of Georgia
P.O. Box 748
Tifton, Georgia 31793

The data sets can be made available on tape, or floppy disk (5-1/4 or 3-1/2 inch). Data sets will be in ASCII format.

An example of the water sample data set is given in Table B.1 The water sample data set also contains data on the elevation of the water table at each well that was sampled. This data set contains over 900 records. An example of the soil sample data set is presented in Table B.2. This data set contains approximately 240 records.

Table B.1 Example listing of the water sample data set.

Sample Date	Station ID	Water Table Elevation (m)	Chemical Concentration (mg/l)			
			Atrazine	Bromide	Nitrate	Chloride
5/25/87	08-09	27.46	0.006	0.01	0.47	13.3
5/25/87	08-10	27.26	0.005	0.04	3.52	41.5
5/25/87	08-11	26.92	0.013	0.00	0.00	82.3
5/25/87	08-12	25.97	.[1]	.	.	.
5/25/87	08-13	25.60	0.011	0.02	0.11	22.87

[1]No sample

Table B.2 Example listing of the soil sample data set.

Sample Date	Sample Location	Depth (cm)	Concentration (mg/kg) Atrazine	Alachlor
5/25/87	1	0-6	0.04	0.02
5/25/87	2	0-6	0.05	0.12
5/25/87	3	0-6	0.03	0.27
5/25/87	4	0-6	0.04	0.17
5/25/87	5	0-6	0.04	0.06
5/25/87	6	0-6	0.04	0.11
5/25/87	7	0-6	0.04	0.12

APPENDIX C

WATER BALANCE PROGRAMS

Figure C.1 Listing of program to calculate water and chemical fluxes and storages.

```
CCCCCCC
C  PROGRAM TO CALCULATE WATER AND CHEMICAL FLUXES AND STORAGES FROM
C  GRIDDED WATER TABLE ELEVATION DATA
C  WRITTEN: 11/22/87   BY: MATT C. SMITH
C  LAST UPDATE:  4/12/88
CCCCCC
      PROGRAM ANALYZE
      REAL WT(23,45),WIMIN,WIMAX,MEANWID(7),KD,BULKDEN
      REAL MAGNITUDE(23,45),DELX,DELY,ANGLE(23,45),MAGMIN,MAGMAX
      REAL SLPX(23,45),SLPY(23,45),DIRECTION(23,45),SURFMAX
      REAL SURF(23,45),SURFMIN,ROW,COL,MAXSTOR(23,45),DRVOL(23,46)
      REAL IMP(23,45),XMIN,XMAX,YMIN,YMAX,IMPMAX,IMPMIN,XPOS,YPOS
      REAL WID(23,45),WIDMIN,WIDMAX,SLPXMAX,SLPYMAX,SLPXMIN,SLPYMIN
      REAL VELX(23,45),VELY(23,45),FLOWXMAX,FLOWYMAX,FLOWXMIN,FLOWYMIN
      REAL FLOWX(23,45),FLOWY(23,45),BFLOWX1(7),BFLOWX2(7),BFLOWY(7)
      REAL NETFLOW(7),AREA(7),COND(45),PORO,NODECOND(7)
      REAL WMASS(23,45),CMASS(23,45),CONC(23,45),TCMASS(7),CFLOWYMIN
      REAL BCFLOWX1(7),BCFLOWX2(7),BCFLOWY(7),NETCFLOW(7),TWMASS(7)
      REAL CONCMIN,CONCMAX,CMASSMAX,CMASSMIN,CWMASS(23,45),CSMASS(23,45)
      REAL CFLOWX(23,45),CFLOWY(23,45),CFLOWXMAX,CFLOWXMIN,CFLOWYMAX
      REAL DRVOLMAX,DRVOLMIN,DRVOLSUM(7),MSTORSUM(7),TEMP
      INTEGER*2 NX,NY,I,J,INC,II,JJ,KK,LL,MM,NN,YY(7),XX(2),SIRT,STP
      INTEGER*2 IYR,IMON,IDAY,IHR,IMIN,ISEC,I100TH,IOUT
      CHARACTER*2 MONTH,DAY,YEAR
      CHARACTER*8 DATE,CHEMFILE
      CHARACTER*12 INFILE1,INFILE2,INFILE3,INFILE4,INFILE6,OUTFILE
      CHARACTER*12 FLUXFILE,COMMENT(14)
CCCCCC
C  INITIALIZE VARIABLES
C  PI = PI
C  COND(J) = SAT. HYDRAULIC CONDUCTIVITY (m/day) AT NODE J
C  NODECOND(J) = SAT. HYDRUALIC COND. AT SPECIFIED NODES J
C  PORO = SOIL POROSITY (cm/cm)
C  KD = PESTICIDE DISTRIBUTION COEFF. (cm**3/g)
C  BULKDEN = SOIL BULK DENSITY (g/cm**3)
CCCCCC
      PI = 3.141592654
      PORO = 0.36
      KD = 0.0489
      BULKDEN = 1.59
      INFILE1 = 'IMPERMBA.GRD'
      INFILE3 = 'SURFACEA.GRD'
      INFILE2 = 'INFILE  .DAT'
CCCCCC
C  FILE INFILE.DAT CONTAINS MONTH, DAY, YEAR VALUES FOR GENERATING
C  FILENAMES AND DATE
C  FILE IMPERMBA.GRD CONTAINS GRIDDED ELEVATIONS OF IMPERMEABLE LAYER
C  FILE SURFACEA.GRD CONTAINS GRIDDED ELEVATIONS OF SOIL SURFACE
CCCCCC
```

Figure C.1 Continued.

```
      OPEN(UNIT=1,FILE=INFILE1,STATUS='OLD')
      OPEN(UNIT=3,FILE=INFILE3,STATUS='OLD')
      OPEN(UNIT=2,FILE=INFILE2,STATUS='OLD')
CCCCCC
C  READ IN IMPERMEABLE LAYER ELEVATION DATA
C  NX,NY ARE # OF X AND Y VALUES IN GRID
C  XMIN, YMIN AND XMAX, YMAX ARE MIN AND MAX VALUES ON RESPECTIVE AXIS
CCCCCC
       READ(1,*)
       READ(1,*) NX,NY
       READ(1,*) XMIN,XMAX
       READ(1,*) YMIN,YMAX
       READ(1,*) IMPMIN,IMPMAX
        DO 5, J= 1,NY
        READ(1,*) (IMP(I,J), I=1,NX)
        READ(1,*)
5      CONTINUE
CCCCCCC
C  CALCULATE SPACING OF GRID POINTS IN X AND Y DIRECTIONS
C  DELX = DISTANCE BETWEEN NODES ON X-AXIS
C  DELY = DISTANCE BETWEEN NODES ON Y-AXIS
CCCCCCC
       DELX = (XMAX-XMIN) / (NX-1)
       DELY = (YMAX-YMIN) / (NY-1)
CCCCCC
C  READ IN SOIL SURFACE ELEVATION DATA
CCCCCC
       READ(3,*)
       READ(3,*)
       READ(3,*)
       READ(3,*)
       READ(3,*) SURFMIN,SURFMAX
        DO 10, J= 1,NY
        READ(3,*) (SURF(I,J), I=1,NX)
        READ(3,*)
10      CONTINUE
CCCCCC
C  READ IN :
C  OUTPUT INCREMENT VALUE, PRINT EVERY INC NODES IN X AND Y
C  CONDUCTIVITY (m/day) AT Y-AXIS BOUNDARY NODES
C  BOUNDARY NODE NUMBERS ON X-AXIS FOR SUBAREA BOUNDARIES, 2 VALUES
C  BOUNDARY NODE NUMBERS ON Y-AXIS FOR SUBAREA BOUNDARIES, 5 VALUES
C  SUMMARY FILE NAME
C  ..AND FOR 28 FILES READ THE FOLLOWING...
C  MONTH, DAY, YEAR AND CHEMICAL FILENAME
CCCCCC
C  CREATE INPUT AND OUTPUT FILENAMES BY ADDING APPROPRIATE EXTENSIONS
CCCCCC
      READ(2,102)INC,IOUT
      READ(2,104)(NODECOND(I),I=1,7)
```

Figure C.1 Continued.

```
      READ(2,102)XX(1),XX(2)
      READ(2,102)(YY(I),I=1,7)
      READ(2,108)FLUXFILE
      READ(2,933)(COMMENT(I),I=1,14)
CCCCCC
C  INTERPOLATE CONDUCTIVITIES AT EACH Y NODE
CCCCCC
      DO 621, I = 1,45
       DO 621, J = 1,6
       IF(I.GE.YY(J).AND.I.LE.YY(J+1)) THEN
        COND(I) = NODECOND(J) + FLOAT(I-YY(J))*(NODECOND(J+1) -
     # NODECOND(J)) / (YY(J+1) - YY(J))
       ELSEIF(I.LE.YY(1)) THEN
        COND(I) = NODECOND(1)
       ELSEIF(I.GE.YY(7)) THEN
        COND(I) = NODECOND(7)
       ENDIF
621    CONTINUE
CCCCCC
C OPEN OUTPUT FILE FOR TRANSFER OF DATA TO WEEKLY FLUX CALCULATION
C PROGRAM
CCCCCC
      OPEN(UNIT=7,FILE=FLUXFILE,STATUS='UNKNOWN')
      WRITE(7,934)(COMMENT(I),I=1,14)
      CALL GETTIM(IHR,IMIN,ISEC,I100TH)
      CALL GETDAT(IYR,IMON,IDAY)
      WRITE(7,171) IMON,IDAY,IYR,IHR,IMIN,ISEC,I100TH
      WRITE(7,195)(NODECOND(I),I=1,7)
      WRITE(7,196)PORO
      WRITE(7,921)KD
      WRITE(7,922)BULKDEN
      WRITE(7,731)XX(1),XX(2)
      WRITE(7,732)(YY(I),I=1,7)
CCCCCC
C BEGIN MAIN LOOP TO PERFORM CALCULATIONS FOR EACH OF 28 OBSERVATION
C PERIODS
CCCCCC
30    DO 15, K=1,50
       READ(2,100,END=20) MONTH,DAY,YEAR,CHEMFILE
       DATE = MONTH // '/' // DAY // '/' // YEAR
       INFILE4 = MONTH // '-' // DAY // 'ELV' // '.GRD'
       INFILE6 = CHEMFILE // '.GRD'
       OUTFILE = MONTH // '-' // DAY // 'WTD' // '.SUM'
       WRITE(*,*) INFILE4,INFILE6,OUTFILE
CCCCCCC
C  OPEN INPUT AND OUTPUT FILES
CCCCCCC
       OPEN(UNIT=4,FILE=INFILE4,STATUS='OLD')
       OPEN(UNIT=5,FILE=OUTFILE,STATUS='UNKNOWN')
       OPEN(UNIT=6,FILE=INFILE6,STATUS='OLD')
```

Figure C.1 Continued.

```
CCCCCCC
C  READ IN VALUES FROM INPUT FILES
C  WIMIN AND WIMAX ARE MIN AND MAX VALUES OF WT ELEVATION
C  CONCMIN AND CONCMAX ARE MIN AND MAX CHEM CONCENTRATION VALUES
CCCCCCC
       READ(4,*)
       READ(4,*)
       READ(4,*)
       READ(4,*)
       READ(4,*) WIMIN,WIMAX
CCCCCC
       READ(6,*)
       READ(6,*)
       READ(6,*)
       READ(6,*)
       READ(6,*) CONCMIN,CONCMAX
CCCCCC
C  ZERO OUT OLD VALUES AT THE NODES AND READ IN NEW VALUES OF WT(I,J)
C AND CONC(I,J)
CCCCCC
       DO 35 I=1,23
        DO 35 J=1,45
        WT(I,J) = 0.0
        WTD(I,J) = 0.0
        CONC(I,J) =0.0
        SLPX(I,J) = 0.0
        SLPY(I,J) = 0.0
        VELX(I,J) = 0.0
        VELY(I,J) = 0.0
        FLOWX(I,J) = 0.0
        FLOWY(I,J) = 0.0
        CFLOWX(I,J) = 0.0
        CFLOWY(I,J) = 0.0
        MAGNITUDE(I,J) = 0.0
        DIRECTION(I,J) = 0.0
        DRVOL(I,J) = 0.0
        MAXSTOR(I,J) = 0.0
35     CONTINUE
        DO 45, J= 1,NY
        READ(4,*) (WT(I,J), I=1,NX)
        READ(4,*)
        READ(6,*) (CONC(I,J), I=1,NX)
        READ(6,*)
45      CONTINUE
CCCCCC
C  NOW COMPUTE SLOPE AND MAGNITUDE AT INTERIOR NODES USING CENTERED
C  DIFFERENCE TECHNIQUES
C  FIRST COMPUTE SLOPE INDIVIDUALLY IN X AND Y DIRECTIONS
C  MINUS SIGN GIVES ACTUAL SLOPE AND NOT GRADIENT
CCCCCC
```

Figure C.1 Continued.

```
        DO 50, J= 2, (NY-1)
         DO 50, I= 2, (NX-1)
         SLPX(I,J) = -( WT(I+1,J) - WT(I-1,J) ) / ( 2.0*DELX )
         SLPY(I,J) = -( WT(I,J+1) - WT(I,J-1) ) / ( 2.0*DELY )
CCCCCCC
C  COMPUTE MAGNITUDE OF RESULTANT SLOPE
CCCCCCC
         MAGNITUDE(I,J) = SQRT ( SLPX(I,J)**2 + SLPY(I,J)**2 )
CCCCCCC
C  COMPUTE DIRECTION OF RESULTANT SLOPE
C  ANGLE IS MEASURED wrt +X AXIS, ie ANGLE = 90 = +Y AXIS
CCCCCCC
         ANGLE(I,J) = ATAN2 ( SLPY(I,J), SLPX(I,J) ) * 180.0 / PI
          IF (ANGLE(I,J).LT.0.0) THEN
            DIRECTION(I,J) = 360.0 + ANGLE(I,J)
           ELSE
            DIRECTION(I,J) = ANGLE(I,J)
           ENDIF
CCCCCC
C  CALCULATE WATER TABLE DEPTH (cm) AT EACH NODE
CCCCCC
      WTD(I,J) = 100.0 * (WT(I,J) - IMP(I,J))
CCCCCC
C  CALCULATE DRAINED VOLUME (m**3) AT EACH NODE
CCCCCC
      WTDEPTH = SURF(I,J) - WT(I,J)
      DRVOL(I,J) = VOLDRAIN(WTDEPTH) * DELX * DELY / 100.0
CCCCCC
C  CALCULATE MAXIMUM STORAGE VOLUME (m**3) AT EACH NODE
CCCCCC
      MAXSTOR(I,J) = (SURF(I,J) - IMP(I,J)) * PORO * DELX * DELY
CCCCCC
C  CALCULATE  VELOCITY, AND FLOWRATE IN X AND Y DIRECTIONS
C  AT EACH NODE.
C  VELX(I,J) = VELOCITY IN X-DIRECTION (m/day)
C  FLOWX(I,J) = VOLUMETRIC FLOWRATE IN X-DIRECTION (m**3/day)
CCCCCC
      VELX(I,J) = COND(J) * SLPX(I,J) / PORO
      VELY(I,J) = COND(J) * SLPY(I,J) / PORO
      FLOWX(I,J) = COND(J) * SLPX(I,J) * DELX * WTD(I,J) / 100.0
      FLOWY(I,J) = COND(J) * SLPY(I,J) * DELY * WTD(I,J) / 100.0
      CFLOWX(I,J) = CONC(I,J) * FLOWX(I,J)
      CFLOWY(I,J) = CONC(I,J) * FLOWY(I,J)
CCCCCC
C  CALCULATE MASS OF WATER AND CHEMICAL AT EACH NODE
C  WMASS = WATER STORAGE IN SATURATED ZONE (m**3) IN NODAL AREA
C  CWMASS = MASS OF CHEMICAL IN WATER (mg) IN NODAL AREA
C  CSMASS = MASS OF CHEMICAL ON SOIL  (mg) IN NODAL AREA
C  CMASS =  TOTAL MASS OF CHEMICAL   (mg)   "    "    "
CCCCCC
```

Figure C.1 Continued.

```
      WMASS(I,J) = WID(I,J) * PORO * DELX * DELY / 100.0
      CWMASS(I,J) = WMASS(I,J) * CONC(I,J)
      CSMASS(I,J) = CWMASS(I,J) * KD * BULKDEN / PORO
      CMASS(I,J) = CWMASS(I,J) + CSMASS(I,J)
CCCCCC
C  CALCULATE MAX AND MIN VALUES OF SELECTED PARAMETERS
CCCCCC
       IF(I.EQ.2.AND.J.EQ.2) THEN
       WIDMAX = WID(2,2)
       WIDMIN = WID(2,2)
       SLPXMAX = SLPX(2,2)
       SLPXMIN = SLPX(2,2)
       SLPYMAX = SLPY(2,2)
       SLPYMIN = SLPY(2,2)
       MAGMAX = MAGNITUDE(2,2)
       MAGMIN = MAGNITUDE(2,2)
       FLOWXMAX = FLOWX(2,2)
       FLOWXMIN = FLOWX(2,2)
       FLOWYMAX = FLOWY(2,2)
       FLOWYMIN = FLOWY(2,2)
       CFLOWXMAX = CFLOWX(2,2)
       CFLOWXMIN = CFLOWX(2,2)
       CFLOWYMAX = CFLOWY(2,2)
       CFLOWYMIN = CFLOWY(2,2)
       CMASSMAX = CMASS(2,2)
       CMASSMIN = CMASS(2,2)
       ENDIF
         IF(WID(I,J).GT.WIDMAX) WIDMAX = WID(I,J)
         IF(WID(I,J).LT.WIDMIN) WIDMIN = WID(I,J)
         IF(SLPX(I,J).LT.SLPXMIN) SLPXMIN = SLPX(I,J)
         IF(SLPX(I,J).GT.SLPXMAX) SLPXMAX = SLPX(I,J)
         IF(SLPY(I,J).LT.SLPYMIN) SLPYMIN = SLPY(I,J)
         IF(SLPY(I,J).GT.SLPYMAX) SLPYMAX = SLPY(I,J)
         IF(MAGNITUDE(I,J).GT.MAGMAX) MAGMAX = MAGNITUDE(I,J)
         IF(MAGNITUDE(I,J).LT.MAGMIN) MAGMIN = MAGNITUDE(I,J)
         IF(FLOWX(I,J).GT.FLOWXMAX) FLOWXMAX = FLOWX(I,J)
         IF(FLOWX(I,J).LT.FLOWXMIN) FLOWXMIN = FLOWX(I,J)
         IF(FLOWY(I,J).GT.FLOWYMAX) FLOWYMAX = FLOWY(I,J)
         IF(FLOWY(I,J).LT.FLOWYMIN) FLOWYMIN = FLOWY(I,J)
         IF(CFLOWX(I,J).GT.CFLOWXMAX) CFLOWXMAX = CFLOWX(I,J)
         IF(CFLOWX(I,J).LT.CFLOWXMIN) CFLOWXMIN = CFLOWX(I,J)
         IF(CFLOWY(I,J).GT.CFLOWYMAX) CFLOWYMAX = CFLOWY(I,J)
         IF(CFLOWY(I,J).LT.CFLOWYMIN) CFLOWYMIN = CFLOWY(I,J)
         IF(CMASS(I,J).GT.CMASSMAX) CMASSMAX = CMASS(I,J)
         IF(CMASS(I,J).LT.CMASSMIN) CMASSMIN = CMASS(I,J)
CCCCCC
C  END NODAL CALCULATION LOOPS
CCCCCC
50        CONTINUE
```

Figure C.1 Continued.

```
CCCCCC
C  BEGIN CALCULATIONS FOR SUB-AREAS AND TOTAL CONTROL AREA
CCCCCC
C  CALCULATE MASS FLOWS ACCROSS BOUNDARIES OF THE SIX AREAS
C  BFLOWX1(I) = FLOW ACCROSS PLANES  WITH X = XX(1), Y = YY(I) TO YY(I+1)
C  BFLOWX2(I) = FLOW ACCROSS PLANES  WITH X = XX(2), Y = YY(I) TO YY(I+1)
C  BFLOWY(I) = FLOW ACCROSS PLANES WITH Y = YY(I), X = XX(1) TO XX(2)
CCCCCC
C  FIRST FLOWS ACCROSS Y PLANES
CCCCCC
      DO 200, KK = 1,7
      BFLOWY(KK) = 0.0
      BCFLOWY(KK) = 0.0
       DO 200, LL = XX(1),XX(2)
         IF(LL.EQ.XX(1).OR.LL.EQ.XX(2)) THEN
C         **HALF AREA CONTRIBUTING ON BOUNDARIES**
          BFLOWY(KK) = BFLOWY(KK) + FLOWY(LL,YY(KK))/2.0
          BCFLOWY(KK) = BCFLOWY(KK) + CFLOWY(LL,YY(KK))/2.0
         ELSE
          BFLOWY(KK) = BFLOWY(KK) + FLOWY(LL,YY(KK))
          BCFLOWY(KK) = BCFLOWY(KK) + CFLOWY(LL,YY(KK))
         ENDIF
200   CONTINUE
CCCCCC
C  NOW FLOWS ACCROSS X-PLANES
CCCCCC
      DO 210, KK = 1,7
      BFLOWX1(KK) = 0.0
      BFLOWX2(KK) = 0.0
      BCFLOWX1(KK) = 0.0
      BCFLOWX2(KK) = 0.0
        STRT = YY(KK)
        STP = YY(KK+1)
        IF(KK.EQ.7) THEN
        STRT = YY(1)
        STP = YY(7)
        ENDIF
       DO 210 LL = STRT,STP
         IF(LL.EQ.STRT.OR.LL.EQ.STP) THEN
C          **HALF AREA CONTRIBUTING ON BOUNDARIES**
          BFLOWX1(KK) = BFLOWX1(KK) + FLOWX(XX(1),LL)/2.0
          BFLOWX2(KK) = BFLOWX2(KK) + FLOWX(XX(2),LL)/2.0
          BCFLOWX1(KK) = BCFLOWX1(KK) + CFLOWX(XX(1),LL)/2.0
          BCFLOWX2(KK) = BCFLOWX2(KK) + CFLOWX(XX(2),LL)/2.0
         ELSE
          BFLOWX1(KK) = BFLOWX1(KK) + FLOWX(XX(1),LL)
          BFLOWX2(KK) = BFLOWX2(KK) + FLOWX(XX(2),LL)
          BCFLOWX1(KK) = BCFLOWX1(KK) + CFLOWX(XX(1),LL)
          BCFLOWX2(KK) = BCFLOWX2(KK) + CFLOWX(XX(2),LL)
         ENDIF
```

Figure C.1 Continued.

```
210   CONTINUE
CCCCCC
C  CALCULATE NET MASS FLUXES IN EACH OF THE SIX SUB-AREAS AND FOR TOTAL
C  AREA.
CCCCCC
      DO 220, MM = 1,6
      NETFLOW(MM)=BFLOWY(MM) + BFLOWX1(MM) - BFLOWX2(MM) - BFLOWY(MM+1)
      NETCFLOW(MM)=BCFLOWY(MM) + BCFLOWX1(MM) - BCFLOWX2(MM) -
     # BCFLOWY(MM+1)
220   CONTINUE
      NETFLOW(7) = BFLOWY(1) + BFLOWX1(7) - BFLOWX2(7) - BFLOWY(7)
      NETCFLOW(7) = BCFLOWY(1) + BCFLOWX1(7) - BCFLOWX2(7) - BCFLOWY(7)
CCCCCCC
C  COMPUTE MEAN WID, TOTAL WATER AND CHEMICAL MASSES IN EACH AREA
CCCCCCC
      DO 310, KK = 1,7
      TWMASS(KK) = 0.0
      TCMASS(KK) = 0.0
      DRVOLSUM(KK) = 0.0
      MSTORSUM(KK) = 0.0
      MEANWID(KK) = 0.0
      AREA(KK)=0.0
      STRT = YY(KK)
      STP = YY(KK+1)
       IF(KK.EQ.7) THEN
       STRT = YY(1)
       STP = YY(7)
       ENDIF
        DO 300, J = STRT,STP
          DO 300, I = XX(1),XX(2)
        IF(I.EQ.XX(1).OR.I.EQ.XX(2)) THEN
          IF(J.EQ.STRT.OR.J.EQ.STP) THEN
C          ** QUARTER AREA CONTRIBUTION IN CORNERS **
           TWMASS(KK) = TWMASS(KK) + WMASS(I,J)/4.0
           TCMASS(KK) = TCMASS(KK) + CMASS(I,J)/4.0
           MSTORSUM(KK) = MSTORSUM(KK) + MAXSTOR(I,J)/4.0
           DRVOLSUM(KK) = DRVOLSUM(KK) + DRVOL(I,J)/4.0
           AREA(KK) = AREA(KK) + DELX * DELY / 4.0
           MEANWID(KK) = MEANWID(KK) + WID(I,J)*DELX*DELY/4.0
C         WRITE(5,951)KK,I,J,TWMASS(KK),WMASS(I,J)
C951        FORMAT(1X,3I3,2(4X,F10.5),'  QUARTER AREA')
          ELSE
C         **HALF AREA CONTRIBUTING ON BOUNDARIES**
          TWMASS(KK) = TWMASS(KK) + WMASS(I,J)/2.0
          TCMASS(KK) = TCMASS(KK) + CMASS(I,J)/2.0
          MSTORSUM(KK) = MSTORSUM(KK) + MAXSTOR(I,J)/2.0
          DRVOLSUM(KK) = DRVOLSUM(KK) + DRVOL(I,J)/2.0
          AREA(KK) = AREA(KK) + DELX * DELY / 2.0
          MEANWID(KK) = MEANWID(KK) + WID(I,J)*DELX*DELY/2.0
C          WRITE(5,952)KK,I,J,TWMASS(KK),WMASS(I,J)
```

Figure C.1 Continued.

```
C952          FORMAT(1X,3I3,2(4X,F10.5),'  HALF AREA')
             ENDIF
            ELSEIF(J.EQ.STRT.OR.J.EQ.STP) THEN
              IF(I.EQ.XX(1).OR.I.EQ.XX(2)) THEN
              GO TO 300
              ELSE
              TWMASS(KK) = TWMASS(KK) + WMASS(I,J)/2.0
              TCMASS(KK) = TCMASS(KK) + CMASS(I,J)/2.0
              MSTORSUM(KK) = MSTORSUM(KK) + MAXSTOR(I,J)/2.0
              DRVOLSUM(KK) = DRVOLSUM(KK) + DRVOL(I,J)/2.0
              AREA(KK) = AREA(KK) + DELX * DELY / 2.0
              MEANWID(KK) = MEANWID(KK) + WID(I,J)*DELX*DELY/2.0
C             WRITE(5,952)KK,I,J,TWMASS(KK),WMASS(I,J)
              ENDIF
             ELSE
             TWMASS(KK) = TWMASS(KK) + WMASS(I,J)
             TCMASS(KK) = TCMASS(KK) + CMASS(I,J)
             MSTORSUM(KK) = MSTORSUM(KK) + MAXSTOR(I,J)
             DRVOLSUM(KK) = DRVOLSUM(KK) + DRVOL(I,J)
             AREA(KK) = AREA(KK) + DELX * DELY
             MEANWID(KK) = MEANWID(KK) + WID(I,J)*DELX*DELY
C             WRITE(5,953)KK,I,J,TWMASS(KK),WMASS(I,J)
C953          FORMAT(1X,3I3,2(4X,F10.5),'  FULL AREA')
            ENDIF
300        CONTINUE
           MEANWID(KK) = MEANWID(KK) / AREA(KK)
310        CONTINUE
CCCCCC
C  WRITE NODAL VALUES TO OUTPUT FILE
C  XPOS AND YPOS ARE THE X AND Y POSITIONS IN THE FIELD IN METERS
C  ROW AND COL CORRESPOND TO THE STATION ID LOCATIONS
CCCCCC
      IF(IOUT.GT.0) THEN
      WRITE(5,110) DATE
C     WRITE(5,623)(COND(I),I=1,45)
C623   FORMAT(10F7.2)
      WRITE(5,120)
          DO 60, J= 2, (NY-1), INC
           DO 60, I= 2, (NX-1), INC
           IF(J.EQ.14.AND.INC.GT.1.AND.I.EQ.2) THEN
             JJ = 11
             DO 80 II = 10,18,4
             XPOS = FLOAT(II-1) * DELX + XMIN
             YPOS = FLOAT(JJ-1) * DELY + YMIN
             ROW = 6.0 + FLOAT (II-2) / 4.0
             COL = 7.0 + FLOAT (JJ-2) / 4.0
          WRITE(5,130)II,JJ,ROW,COL,XPOS,YPOS,SURF(II,JJ),IMP(II,JJ),
     #    WT(II,JJ),WID(II,JJ),SLPX(II,JJ),SLPY(II,JJ),MAGNITUDE(II,JJ),
     #    DIRECTION(II,JJ)
80           CONTINUE
```

Figure C.1 Continued.

```
            ENDIF
            XPOS = FLOAT(I-1) * DELX + XMIN
            YPOS = FLOAT(J-1) * DELY + YMIN
            ROW = 6.0 + FLOAT (I-2) / 4.0
            COL = 7.0 + FLOAT (J-2) / 4.0
            WRITE(5,130)I,J,ROW,COL,XPOS,YPOS,SURF(I,J),IMP(I,J),
     # WT(I,J),WID(I,J),SLPX(I,J),SLPY(I,J),MAGNITUDE(I,J),
     # DIRECTION(I,J)
60     CONTINUE
       WRITE(5,140)
       WRITE(5,431)
       WRITE(5,432)
       WRITE(5,433)
           DO 320, J= 2, (NY-1), INC
            DO 320, I= 2, (NX-1), INC
            IF(J.EQ.14.AND.INC.GT.1.AND.I.EQ.2) THEN
              JJ = 11
              DO 380 II = 10,18,4
              WRITE(5,142)II,JJ,MAXSTOR(II,JJ),DRVOL(II,JJ),WMASS(II,JJ),
     #        CONC(II,JJ),CWMASS(II,JJ),CSMASS(II,JJ),CMASS(II,JJ),
     #        FLOWX(II,JJ),VELX(II,JJ),CFLOWX(II,JJ),FLOWY(II,JJ),
     #        VELY(II,JJ),CFLOWY(II,JJ)
380           CONTINUE
         ENDIF
            WRITE(5,142)I,J,MAXSTOR(I,J),DRVOL(I,J),WMASS(I,J),CONC(I,J),
     # CWMASS(I,J),CSMASS(I,J),CMASS(I,J),FLOWX(I,J),VELX(I,J),
     # CFLOWX(I,J),FLOWY(I,J),VELY(I,J),CFLOWY(I,J)
320    CONTINUE
CCCCCC
C  WRITE BOUNDARY FLUX AND STORAGE VALUES
CCCCCC
       WRITE(5,140)
       WRITE(5,180)
       WRITE(5,448)(AREA(I),I=1,7)
       WRITE(5,181)(BFLOWX1(I),I=1,7)
       WRITE(5,182)(BFLOWX2(I),I=1,7)
       WRITE(5,183)(BFLOWY(I),I=1,6),BFLOWY(1)
       WRITE(5,421)(BFLOWY(I),I=2,7),BFLOWY(7)
       WRITE(5,187)(NETFLOW(I),I=1,7)
       WRITE(5,412)(MSTORSUM(I),I=1,7)
       WRITE(5,411)(DRVOLSUM(I),I=1,7)
       WRITE(5,191)(TWMASS(I),I=1,7)
       WRITE(5,447)(MEANWID(I),I=1,7)
       WRITE(5,184)(BCFLOWX1(I),I=1,7)
       WRITE(5,185)(BCFLOWX2(I),I=1,7)
       WRITE(5,186)(BCFLOWY(I),I=1,6),BCFLOWY(1)
       WRITE(5,422)(BCFLOWY(I),I=2,7),BCFLOWY(7)
       WRITE(5,188)(NETCFLOW(I),I=1,7)
       WRITE(5,192)(TCMASS(I),I=1,7)
```

Figure C.1 Continued.

```
CCCCCC
C  WRITE MAXIMUMS AND MINIMUMS
CCCCCC
      WRITE(5,149)
      WRITE(5,150)SURFMIN,SURFMAX
      WRITE(5,151)IMPMIN,IMPMAX
      WRITE(5,152)WIMIN,WIMAX
      WRITE(5,153)WIDMIN,WIDMAX
      WRITE(5,154)SLPXMIN,SLPXMAX
      WRITE(5,155)SLPYMIN,SLPYMAX
      WRITE(5,156)MAGMIN,MAGMAX
      WRITE(5,157)FLOWXMIN,FLOWXMAX
      WRITE(5,158)FLOWYMIN,FLOWYMAX
      WRITE(5,163)CFLOWXMIN,CFLOWXMAX
      WRITE(5,164)CFLOWYMIN,CFLOWYMAX
      WRITE(5,165)CMASSMIN,CMASSMAX
      WRITE(5,166)CONCMIN,CONCMAX
CCCCCC
C  POST FILENAMES USED IN THIS ANALYSIS
CCCCCC
      WRITE(5,160)
      WRITE(5,161)INFILE1,OUTFILE
      WRITE(5,162)INFILE2,INFILE3,INFILE4,INFILE6
      WRITE(5,195)(NODECOND(I),I=1,7)
      WRITE(5,196)PORO
      WRITE(5,921)KD
      WRITE(5,922)BULKDEN
      WRITE(5,731)XX(1),XX(2)
      WRITE(5,732)(YY(I),I=1,7)
      WRITE(5,934)(COMMENT(I),I=1,14)
CCCCCC
C  CALL DATE AND TIME TO MARK OUTPUT FOR LATER REFERENCE
CCCCCC
      CALL GETTIM(IHR,IMIN,ISEC,I100TH)
      CALL GETDAT(IYR,IMON,IDAY)
      WRITE(5,170)  IMON,IDAY,IYR,IHR,IMIN,ISEC,I100TH
      ENDIF
CCCCCC
C  WRITE TO FLUX SUMMARY OUTPUT FILE
CCCCCC
      WRITE(7,452)(AREA(I),I=1,7),DATE
      WRITE(7,401)(NETFLOW(I),I=1,7),DATE
      WRITE(7,402)(TWMASS(I),I=1,7),DATE
      WRITE(7,405)(DRVOLSUM(I),I=1,7),DATE
      WRITE(7,406)(MSTORSUM(I),I=1,7),DATE
      WRITE(7,451)(MEANWID(I),I=1,7),DATE
      WRITE(7,403)(NETCFLOW(I),I=1,7),DATE
      WRITE(7,404)(TCMASS(I),I=1,7),DATE
```

Figure C.1 Continued.

```
CCCCCC
C CLOSE FILES
CCCCCC
      CLOSE(UNIT=4,STATUS='KEEP')
      CLOSE(UNIT=5,STATUS='KEEP')
      CLOSE(UNIT=6,STATUS='KEEP')
CCCCCC
C LOOP BACK FOR NEXT FILE
CCCCCC
15    CONTINUE
CCCCCC
C STOP FOR NORMAL TERMINATION
CCCCCC
20    STOP ' END OF FILE ON INFILE.DAT'
CCCCCC
C  FORMAT STATEMENTS
CCCCCC
100   FORMAT(3(A2,1X),A8)
102   FORMAT(10I3)
104   FORMAT(7F10.2)
106   FORMAT(I1)
108   FORMAT(A12)
110   FORMAT(' ',/,45X,'GOPHER RIDGE WATER TABLE DATA',/,52X,'DATE = ',
     # A8,//,2X,118('-'))
120   FORMAT(' ',2X,'NODE  STATION ID   LOCATION  (m)  ----ELEVATION  '
     #'(m)-----  WT DEPTH  ------WATER TABLE SLOPE (m/m)-----  ',
     #'DIRECTION',/,4X,'I  J',17X,'X',7X,'Y',5X,'SURF',4X,'IMP',6X,'WT',
     # 6X,'(cm)',10X,'X',9X,'Y',8X,'MAGNITUDE',2X,'(degrees)',/,
     # 2X,118('-'))
130   FORMAT(' ',1X,I2,1X,I2,2X,F5.2,'-',F5.2,2X,F5.2,2X,F6.2,
     # 3(2X,F6.3),3X,F5.1,4X,3(E10.4,2X),3X,F4.0,4(F7.3,1X))
140   FORMAT(' ',118('-'))
431   FORMAT(1X,126('-'),/,3X,'I  J  MAXIMUM  DRAINED SATURATED  ',
     #'CHEMICAL  CHEMICAL STORAGE  ',2X,8('-'),'X DIRECTION',7('-'),
     #3X,6('-'),'Y DIRECTION',8('-'))
432    FORMAT(10X,'STORAGE  VOLUME  STORAGE  CONC.',6X,
     #'WATER  SOIL  TOTAL  FLOWRATE  VELOCITY CHEMICAL FLOWRATE',
     #' VELOCITY CHEMICAL')
433    FORMAT(9X,'(m**3)  (m**3)  (m**3)  (ppb)  ',3(' (mg) ')
     #,'(m**3/day)',1X,'(m/day) (mg/day) (m**3/day) (m/day) ',
     # '(mg/day)',/,1X,126('-'))
142   FORMAT(2X,I2,2X,I2,3(F9.4),F9.2,9(F9.3))
149   FORMAT(' ',3X,53('-'),/,5X,'PARAMETER',18X,
     # 'MINIMUM',7X,'MAXIMUM',/,5X,53('-'))
150   FORMAT(' ',4X,'SOIL SURFACE ELEVATION',5X,F5.2,9X,F5.2)
151   FORMAT(' ',4X,'IMP. LAYER  ELEVATION',5X,F5.2,9X,F5.2)
152   FORMAT(' ',4X,'WATER TABLE  ELEVATION',5X,F5.2,9X,F5.2)
153   FORMAT(' ',4X,'WATER TABLE DEPTH',9X,F5.1,9X,F5.1)
154   FORMAT(' ',4X,'SLOPE  IN  X-DIRECTION',3X,E10.4,5X,E10.4)
155   FORMAT(' ',4X,'SLOPE  IN  Y-DIRECTION',3X,E10.4,5X,E10.4)
```

Figure C.1 Continued.

```
156   FORMAT(' ',4X,'SLOPE  MAGNITUDE',9X,E10.4,5X,E10.4)
157   FORMAT(' ',4X,'FLOW  IN   X-DIRECTION',3X,E10.4,5X,E10.4)
158   FORMAT(' ',4X,'FLOW  IN   Y-DIRECTION',3X,E10.4,5X,E10.4)
160   FORMAT(' ',4X,53('-'),///,5X,'INPUT FILES',14X,'OUTPUT FILE',/,
     # 5X,11('-'),14X,11('-'))
161   FORMAT(' ',4X,'UNIT 1 = ',A12,4X,'UNIT 5 = ',A12)
162   FORMAT(' ',4X,'UNIT 2 = ',A12,/,5X,'UNIT 3 = ',A12,/,5X,
     # 'UNIT 4 = ',A12,/,5X,'UNIT 6 = ',A12)
163   FORMAT(' ',4X,'CHEM FLOW  IN    X-DIR',3X,E10.4,5X,E10.4)
164   FORMAT(' ',4X,'CHEM FLOW  IN    Y-DIR',3X,E10.4,5X,E10.4)
165   FORMAT(' ',4X,'CHEMICAL MASS  STORAGE',3X,E10.4,5X,E10.4)
166   FORMAT(' ',4X,'CHEMICAL CONCENTRATION',3X,E10.4,5X,E10.4)
170   FORMAT(/,4X,'PROGRAM RUN ON ',I2.2,'/',I2.2,'/',I4,'  AT ',
     # I2.2,'.',I2.2,'.',I2.2,'.'I2.2)
171   FORMAT(4X,'PROGRAM RUN ON ',I2.2,'/',I2.2,'/',I4,'  AT ',
     # I2.2,'.',I2.2,'.',I2.2,'.'I2.2)
180   FORMAT(' '2X,' BOUNDARY FLUXES',/,2X,110('-'))
448   FORMAT(' ',' AREA(I)     ',7(F10.5,2X))
181   FORMAT(' ',' BFLOWX1(I) ',7(F10.5,2X))
182   FORMAT(' ',' BFLOWX2(I) ',7(F10.5,2X))
183   FORMAT(' ',' BFLOWY1(I) ',7(F10.5,2X))
421   FORMAT(' ',' BFLOWY2(I) ',7(F10.5,2X))
184   FORMAT(' ',/,'  BCFLOWX1(I)',7(F10.5,2X))
185   FORMAT(' ',' BCFLOWX2(I)',7(F10.5,2X))
186   FORMAT(' ',' BCFLOWY1(I)',7(F10.5,2X))
422   FORMAT(' ',' BCFLOWY2(I)',7(F10.5,2X))
187   FORMAT(' ',' NETFLOW(I) ',7(F10.5,2X))
188   FORMAT(' ',' NETCFLOW(I)',7(F10.5,2X))
191   FORMAT(' ',' TWMASS(I)   ',7(F10.5,2X))
447   FORMAT(' ',' MEANWID(I) ',7(F10.5,2X))
192   FORMAT(' ',' TCMASS(I)   ',7(F10.5,2X),/,2X,110('-'))
411   FORMAT(' ',' DRVOL(I)    ',7(F10.5,2X))
412   FORMAT(' ',' MAXSTOR(I) ',7(F10.5,2X))
195   FORMAT('     HYD COND. : ',7(F5.2,2X))
196   FORMAT('     POROSITY  : ',F5.2)
401   FORMAT('  NETFLOW(I)  : ',7(F10.5,2X),A8)
452   FORMAT(/,'  AREA(I)     : ',7(F10.5,2X),A8)
402   FORMAT('  TWMASS(I)   : ',7(F10.5,2X),A8)
403   FORMAT('  NETCFLOW(I) : ',7(F10.5,2X),A8)
404   FORMAT('  TCMASS(I)   : ',7(F10.5,2X),A8)
405   FORMAT('  DRVOL(I)    : ',7(F10.5,2X),A8)
406   FORMAT('  MAXSTOR(I)  : ',7(F10.5,2X),A8)
451   FORMAT('  MEANWID(I)  : ',7(F10.5,2X),A8)
731   FORMAT('     X-NODE BOUNDARIES : ',2I3)
732   FORMAT('     Y-NODE BOUNDARIES : ',7I3)
921   FORMAT('     PARTIONING COEFF  : ',F7.5)
922   FORMAT('     BULK DENSITY      : ',F7.3)
933   FORMAT(7A12)
934   FORMAT('     COMMENT  : ',7A12)
```

Figure C.1 Continued.

```
CCCCCC
C THE END !!!!!
CCCCCC
      END
CCCCCC
C  FUNCTION TO CALCULATE THE VOLUME DRAINED IN CM FOR A GIVEN WATER TABLE
C  DEPTH.  FUNCTION CREATED BY USING LINEAR REGRESSION ON THE VOLUME
C  DRAINED - WATER TABLE DEPTH CURVE FOR WT DEPTH VALUES IN THE RANGE
C  OF 1.5 - 3.5 METERS
CCCCCC
      FUNCTION VOLDRAIN(WTDEPTH)
      VOLDRAIN = -12.5887 + 29.048 * WTDEPTH
      RETURN
      END
```

Table C.1. Sample ouput from program ANALYZE.

GOPHER RIDGE WATER TABLE DATA

DATE = 5/05/87

NODE I	NODE J	STATION ID	LOCATION X (m)	LOCATION Y (m)	ELEVATION SURF	ELEVATION IMP	ELEVATION WT	WT DEPTH (cm)	WATER TABLE SLOPE X	WATER TABLE SLOPE Y	SLOPE MAGNITUDE (m/m)	DIRECTION (degrees)
2	2	6.00- 7.00	.00	73.15	30.420	27.710	28.037	32.7	-.5500E-02	-.1263E-02	.5643E-02	193.
6	2	7.00- 7.00	12.19	73.15	30.405	27.770	27.997	22.7	.5601E-02	-.6131E-02	.8304E-02	312.
10	2	8.00- 7.00	24.38	73.15	30.400	28.000	28.000	.0	-.7234E-02	-.8363E-02	.1106E-01	229.
14	2	9.00- 7.00	36.58	73.15	30.334	27.945	28.094	14.9	-.2259E-02	-.1603E-01	.1618E-01	262.
18	2	10.00- 7.00	48.77	73.15	30.270	27.951	28.112	16.1	-.4843E-02	-.7401E-02	.8845E-02	237.
22	2	11.00- 7.00	60.96	73.15	30.240	28.110	28.230	12.0	-.5080E-02	-.7938E-02	.9424E-02	237.
2	6	6.00- 8.00	.00	85.34	30.368	27.593	27.937	34.3	.2883E-02	.1717E-02	.3356E-02	31.
6	6	7.00- 8.00	12.19	85.34	30.376	27.606	27.933	32.7	-.1626E-02	.1012E-01	.1025E-01	99.
10	6	8.00- 8.00	24.38	85.34	30.383	27.789	28.024	23.5	-.1604E-01	.7099E-02	.1754E-01	156.
14	6	9.00- 8.00	36.58	85.34	30.410	28.020	28.218	19.9	-.2878E-02	.6295E-02	.6921E-02	115.
18	6	10.00- 8.00	48.77	85.34	30.320	27.926	28.142	21.6	.3308E-02	.5636E-02	.6535E-02	60.
22	6	11.00- 8.00	60.96	85.34	30.261	28.022	28.189	16.7	-.7888E-02	-.3624E-02	.8681E-02	205.

I	J	MAXIMUM STORAGE (m**3)	DRAINED VOLUME (m**3)	SATURATED STORAGE (m**3)	CHEMICAL CONC. (ppb)	CHEMICAL WATER (mg)	CHEMICAL SOIL (mg)	CHEMICAL TOTAL (mg)	STORAGE X DIRECTION FLOWRATE (m**3/day)	STORAGE X DIRECTION VELOCITY (m/day)	STORAGE X DIRECTION CHEMICAL (mg/day)	STORAGE Y DIRECTION FLOWRATE (m**3/day)	STORAGE Y DIRECTION VELOCITY (m/day)	STORAGE Y DIRECTION CHEMICAL (mg/day)
2	2	9.0636	5.2613	1.0937	17.38	19.010	4.106	23.116	-.077	-.214	-1.334	-.018	-.049	-.306
6	2	8.8152	5.3305	.7595	20.64	15.676	3.386	19.062	.054	.218	1.120	-.059	-.238	-1.226
10	2	8.0269	5.3073	.0000	22.03	.000	.000	.000	.000	-.281	.000	.000	-.325	.000
14	2	7.9896	4.8762	.4970	19.05	9.466	2.044	11.510	-.014	-.088	-.273	-.102	-.623	-1.936
18	2	7.7569	4.6551	.5383	14.72	7.922	1.711	9.633	-.033	-.188	-.490	-.051	-.288	-.748
22	2	7.1239	4.2553	.4007	11.89	4.762	1.029	5.791	-.026	-.198	-.309	-.041	-.309	-.482
2	6	9.2798	5.3920	1.1479	17.50	20.083	4.337	24.421	.042	.112	.739	.025	.067	.440
6	6	9.2629	5.4230	1.0926	25.47	27.830	6.011	33.841	-.023	-.063	-.577	.141	.394	3.595
10	6	8.6776	5.1975	.7867	32.77	25.785	5.569	31.354	-.161	-.624	-5.276	.071	.276	2.335
14	6	7.9938	4.7446	.6642	22.91	15.215	3.286	18.500	-.024	-.112	-.559	.053	.245	1.222
18	6	8.0052	4.7072	.7220	12.93	9.334	2.016	11.350	.030	.129	.394	.052	.219	.671
22	6	7.4898	4.4228	.5591	9.74	5.448	1.177	6.625	-.056	-.307	-.548	-.026	-.141	-.252

Table C.1. Continued.

BOUNDARY FLUXES

AREA(I)	1430.70500	1226.31900	1226.31900	1226.31900	817.54620	817.54620	6744.80800
BFLOWX1(I)	.00000	.00000	.00000	.00000	.00000	.00000	.00000
BFLOWX2(I)	.00000	.00000	.00000	.00000	.00000	.00000	.00000
BFLOWY1(I)	.00000	1.77918	4.17766	17.00191	19.74327	14.53423	.00000
BFLOWY2(I)	1.77918	4.17766	17.00191	19.74327	14.53423	21.56270	21.56270
NETFLOW(I)	-1.77918	-2.39848	-12.82425	-2.74135	5.20904	-7.02847	-21.56270
MAXSTOR(I)	1142.99300	1089.65600	1074.21200	1269.00300	917.17760	944.13010	6437.17500
DRVOL(I)	682.37870	628.29070	628.39540	780.16060	578.92000	604.75040	3902.89800
TWMASS(I)	99.45535	128.36940	112.79580	119.49960	77.95414	72.89392	610.96830
MEANWTD(I)	19.30970	29.07741	25.54977	27.06828	26.48648	24.76717	25.16207
BCFLOWX1(I)	.00000	.00000	.00000	.00000	.00000	.00000	.00000
BCFLOWX2(I)	.00000	.00000	.00000	.00000	.00000	.00000	.00000
BCFLOWY1(I)	.00000	69.81870	30.65918	7.25275	.00000	.00000	.00000
BCFLOWY2(I)	69.81870	30.65918	7.25275	.00000	.00000	.00000	.00000
NETCFLOW(I)	-69.81870	39.15952	23.40643	7.25275	.00000	.00000	.00000
TCMASS(I)	2540.22400	3290.70000	446.42620	8.06712	.00000	.00000	6285.41500

PARAMETER	MINIMUM	MAXIMUM
SOIL SURFACE ELEVATION	22.12	30.42
IMP. LAYER ELEVATION	20.72	28.17
WATER TABLE ELEVATION	21.22	28.28
WATER TABLE DEPTH	.0	75.0
SLOPE IN X-DIRECTION	-.7606E-01	.5374E-01
SLOPE IN Y-DIRECTION	-.1603E-01	.1070E+00
SLOPE MAGNITUDE	.1089E-02	.1186E+00
FLOW IN X-DIRECTION	-.1208E+01	.7787E+00
FLOW IN Y-DIRECTION	-.1665E+00	.2049E+01
CHEM FLOW IN X-DIR	-.3292E+02	.1587E+02
CHEM FLOW IN Y-DIR	-.2325E+01	.3688E+02
CHEMICAL MASS STORAGE	.0000E+00	.9983E+02
CHEMICAL CONCENTRATION	.0000E+00	.8900E+02

Table C.1. Continued.

```
- - - - - - - - - - - - - - - - - - - - - - - - - - -
INPUT FILES                 OUTPUT FILE
-----------                 -----------
UNIT 1 = IMPERMBA.GRD       UNIT 5 =  5-05WTD.SUM
UNIT 2 = INFILE  .DAT
UNIT 3 = SURFACEA.GRD
INPUT FILES                 OUTPUT FILE
-----------                 -----------
UNIT 4 =  5-05ELV.GRD
UNIT 6 = 5-05ATRS.GRD
HYD COND. : 14.00  14.00  14.00  14.00  14.00  14.00  14.00  14.00
POROSITY  :   .36
PARTIONING COEFF  :  .04890
BULK DENSITY      :  1.590
X-NODE BOUNDARIES :  1 23
Y-NODE BOUNDARIES :  1  8 14 20 26 30 34
COMMENT  : CONSTANT HYD. CONDUCTIVITY = 14 m/day
COMMENT  : USING ATRAZINE DATA W/O FORCED ZERO CONCENTRATIONS, WHOLE SITE
PROGRAM RUN ON 06/06/1988  AT 21.52.27.50
```

Figure C.2 Program to calculate mass balances between sampling periods.

```
CCCCCC
C  PROGRAM TO ANALYZE MASS BALANCES BETWEEN SUCCESSIVE SAMPLING PERIODS
C  CREATED: 1/3/88  BY: MATT C. SMITH
C  LAST UPDATE:  4/6/88
CCCCCC
      REAL NETWFLOW(28,7),NETCFLOW(28,7),TWMASS(28,7),TCMASS(28,7)
      REAL CERROR(28,7),WERROR(28,7),AVGWFLOW(28,7),AVGCFLOW(28,7)
      REAL DELWMASS(28,7),DELCMASS(28,7),AREA(7),PERC(28)
      REAL PDELWMASS(28,7),PDELCMASS(28,7),DRVOLSUM(28,7),MSTORSUM(28,7)
      REAL MEANWTD(28,7),DELTAWTD(28,7),WERRORP(28,7),CERRORP(28,7)
      REAL TOTWERROR(7),TOTCERROR(7),CFLUX(28),APPAREA
      INTEGER I,J,DAY(28),NFILE
      CHARACTER*8 DATE(28)
      CHARACTER*12 INFILE,INFILE2,OUTFILE,COMMENTS(100)
CCCCCC
C APPAREA = APPLICATION AREA SIZE (ha)
CCCCCC
      APPAREA = 0.02787
CCCCCC
C  READ IN INPUT AND OUTPUT FILENAMES
CCCCCC
      OPEN(UNIT=1,FILE='INFLUX.DAT',STATUS='OLD')
      READ(1,102)INFILE
      READ(1,108)NFILE
      READ(1,102)INFILE2
      READ(1,102)OUTFILE
102   FORMAT(A12)
108   FORMAT(I2)
CCCCCC
C  OPEN FILES
CCCCCC
      OPEN(UNIT=3,FILE=INFILE,STATUS='OLD')
      OPEN(UNIT=4,FILE=INFILE2,STATUS='OLD')
      OPEN(UNIT=5,FILE=OUTFILE,STATUS='UNKNOWN')
      OPEN(UNIT=7,FILE='SUMMARY.SUM',STATUS='UNKNOWN')
CCCCCC
C  READ IN DATA FROM INPUT FILES
C  DAY(I) = DAYS SINCE APPLICATION
C  PERC(I) = PERCOLATION DURING PERIOD (cm)
C  CFLUX(I) = CHEMICAL FLUX DURING PERIOD (g/ha)
C  AREA(I) = AREA OF SUBAREAS (m**2)
C  NETFLOW(I) = NET WATER FLUX INTO (+) OR OUT OF (-) SUBAREAS (m**3/day)
C  TWMASS(I) = TOTAL WATER IN SUBAREA (m**3)
C  DRVOLSUM(I) = DRAINED VOLUME IN SUBAREA (cm)
C  MSTORSUM(I) = WATER IN SATURATED ZONE IN SUBAREA (m**3)
C  MEANWTD(I) = MEAN WATER TABLE DEPTH IN SUBAREA (CM)
CCCCCC
      READ(3,721)(COMMENTS(I),I=1,54)
      DO 10, I = 1,NFILE
      READ(3,*)
```

Figure C.2 Continued.

```
      READ(3,115)(NETWFLOW(I,J),J=1,7),DATE(I)
      READ(3,115)(TWMASS(I,J),J=1,7),DATE(I)
      READ(3,115)(DRVOLSUM(I,J),J=1,7),DATE(I)
      READ(3,115)(MSTORSUM(I,J),J=1,7),DATE(I)
      READ(3,115)(MEANWTD(I,J),J=1,7),DATE(I)
      READ(3,115)(NETCFLOW(I,J),J=1,7),DATE(I)
      READ(3,115)(TCMASS(I,J),J=1,7),DATE(I)
10    CONTINUE
CCCCCC
C  BEGIN CALCULATIONS
CCCCCC
      WRITE(*,94)
94    FORMAT(' BEGINING CALCULATIONS')
      DO 15, I = 2,NFILE
       DO 15, J = 1,7
CCCCCC
C  CALULATE AVERAGE WATER AND CHEMICAL FLUX IN EACH SUB-AREA BETWEEN
C  SAMPLING DATES
CCCCCCC
       AVGWFLOW(I,J) = (NETWFLOW(I-1,J) + NETWFLOW(I,J)) / 2.0
       AVGCFLOW(I,J) = (NETCFLOW(I-1,J) + NETCFLOW(I,J)) / 2.0
CCCCCC
C  CALCULATE CHANGES IN OBSERVED PARAMETERS BETWEEN DATES
CCCCCC
C      DRAINED VOL @ I GT DRVOL @ I-1 => WATER LOSS
       DELWMASS(I,J) = DRVOLSUM(I-1,J) - DRVOLSUM(I,J)
       DELCMASS(I,J) = TCMASS(I,J) - TCMASS(I-1,J)
       DELTAWTD(I,J) = MEANWTD(I,J) - MEANWTD(I-1,J)
CCCCCC
C  CALULATE PREDICTED CHANGE IN WATER AND CHEMICAL MASS BASED
C  ON AVERAGE FLOWRATES BETWEEN PERIODS
CCCCCC
       PDELWMASS(I,J) = AVGWFLOW(I,J) * FLOAT(DAY(I)-DAY(I-1)) +
     #  (PERC(I)/100.0)*AREA(J)
      IF(J.EQ.2) THEN
       PDELCMASS(I,J) = AVGCFLOW(I,J) * FLOAT(DAY(I)-DAY(I-1)) +
     #  CFLUX(I) * APPAREA * 1000.0
      ELSE
       PDELCMASS(I,J) = AVGCFLOW(I,J) * FLOAT(DAY(I)-DAY(I-1))
      ENDIF
711    FORMAT(A8,4I3,8(F8.3,1X))
CCCCCC
C  CALCULATE DIFFERENCE BETWEEN PREDICTED AND OBSERVED VALUES
CCCCCC
       WERROR(I,J) = PDELWMASS(I,J) - DELWMASS(I,J)
       CERROR(I,J) = PDELCMASS(I,J) - DELCMASS(I,J)
       TOTWERROR(J) = TOTWERROR(J) + WERROR(I,J)
       TOTCERROR(J) = TOTCERROR(J) + CERROR(I,J)
```

Figure C.2 Continued.

```
CCCCCC
C  CALCULATE THE PERCENTAGE ERROR FROM OBSERVED VALUE
CCCCCC
        IF(DELWMASS(I,J).NE.0.0) THEN
          WERRORP(I,J) = 100.0 * WERROR(I,J) / ABS(DELWMASS(I,J))
        ENDIF
        IF(DELCMASS(I,J).NE. 0.0) THEN
          CERRORP(I,J) = 100.0 * CERROR(I,J) / ABS(DELCMASS(I,J))
         ENDIF
15      CONTINUE
CCCCCC
C  WRITE RESULTS TO OUTPUT FILES
CCCCCC
      WRITE(5,125)
      WRITE(5,721)(COMMENTS(I),I=1,54)
      WRITE(7,721)(COMMENTS(I),I=1,54)
        DO 25,I=1,NFILE
        IF(I.EQ.1) THEN
C        FOR 1ST DATA PERIOD THE ARE NO COMPARISONS TO BE PRINTED
         WRITE(5,130)DATE(I),'11/12/86'
         WRITE(5,135)DAY(I),'11/12/86',PERC(I)
         WRITE(5,137)(AREA(J),J=1,7)
         WRITE(5,241)DATE(I),(MSTORSUM(I,J),J=1,7)
         WRITE(5,242)DATE(I),(DRVOLSUM(I,J),J=1,7)
         WRITE(5,145)DATE(I),(TWMASS(I,J),J=1,7)
         WRITE(5,243)DATE(I),(MEANWTD(I,J),J=1,7)
         WRITE(5,140)DATE(I),(NETWFLOW(I,J),J=1,7)
         WRITE(5,136)DAY(I),'11/12/86',CFLUX(I)
         WRITE(5,150)DATE(I),(NETCFLOW(I,J),J=1,7)
         WRITE(5,155)DATE(I),(TCMASS(I,J),J=1,7)
        ELSE
         WRITE(5,130)DATE(I),DATE(I-1)
         WRITE(5,135)DAY(I),DATE(I-1),PERC(I)
         WRITE(5,241)DATE(I),(MSTORSUM(I,J),J=1,7)
         WRITE(5,242)DATE(I),(DRVOLSUM(I,J),J=1,7)
         WRITE(5,145)DATE(I),(TWMASS(I,J),J=1,7)
         WRITE(5,243)DATE(I),(MEANWTD(I,J),J=1,7)
         WRITE(5,140)DATE(I),(NETWFLOW(I,J),J=1,7)
         WRITE(5,141)(AVGWFLOW(I,J),J=1,7)
         WRITE(5,247)(DELTAWTD(I,J),J=1,7)
         WRITE(5,142)(DELWMASS(I,J),J=1,7)
         WRITE(5,143)(PDELWMASS(I,J),J=1,7)
         WRITE(5,144)(WERROR(I,J),J=1,7)
         WRITE(5,177)(WERRORP(I,J),J=1,7)
         WRITE(5,136)DAY(I),DATE(I-1),CFLUX(I)
         WRITE(5,150)DATE(I),(NETCFLOW(I,J),J=1,7)
         WRITE(5,155)DATE(I),(TCMASS(I,J),J=1,7)
         WRITE(5,151)(AVGCFLOW(I,J),J=1,7)
         WRITE(5,152)(DELCMASS(I,J),J=1,7)
         WRITE(5,153)(PDELCMASS(I,J),J=1,7)
```

Figure C.2 Continued.

```
          WRITE(5,154)(CERROR(I,J),J=1,7)
          WRITE(5,178)(CERRORP(I,J),J=1,7)
          WRITE(7,135)DAY(I),DATE(I-1),PERC(I)
          WRITE(7,141)(AVGWFLOW(I,J),J=1,7)
          WRITE(7,142)(DELWMASS(I,J),J=1,7)
          WRITE(7,143)(PDELWMASS(I,J),J=1,7)
         ENDIF
25      CONTINUE
        WRITE(5,436)(TOTWERROR(J),J=1,7)
        WRITE(5,437)(TOTCERROR(J),J=1,7)
        WRITE(7,438)(TOTWERROR(J),J=1,7)
CCCCCC
C  STOP AND END PROGRAM
CCCCCC
      STOP ' END OF PROCCESSING !!!!!'
CCCCCC
C  FORMAT STATEMENTS
CCCCCC
110    FORMAT(I3,3X,2(F10.4))
115    FORMAT(16X,7(F10.5,2X),A8)
125     FORMAT('  SUMMARY OF FLUX DATA',/)
130    FORMAT(/,'  CHANGE BETWEEN ',A8,' AND ',A8)
135    FORMAT('  DAYS SINCE APPLICATION:',I3,', PERCOLATION SINCE ',
     # A8,' = ',F5.2,' cm')
136     FORMAT('  DAYS SINCE APPLICATION:',I3,', CHEMICAL FLUX SINCE ',
     # A8,' = ',F5.2,' mg/m**2')
137    FORMAT('  AREA OF SUBAREA (m^2) : ',8(F10.4,2X))
140    FORMAT('  NETWFLOW ON ',A8,'  : ',8(F10.4,2X))
141    FORMAT('  AVGWFLOW OVER PERIOD  : ',8(F10.4,2X))
142    FORMAT('  DELTA WSTORAGE (m^3)  : ',8(F10.4,2X))
247    FORMAT('  DELTA MEAN WTD (cm)   : ',8(F10.4,2X))
143    FORMAT('  PRED DELTA WSTORAGE   : ',8(F10.4,2X))
144    FORMAT('  ERROR IN WSTORAGE(m^3): ',8(F10.4,2X))
145    FORMAT('  SAT. STORAGE ',A8,' : ',8(F10.4,2X))
242    FORMAT('  DRAINED VOL  ',A8,' : ',8(F10.4,2X))
241    FORMAT('  MAX  STORAGE ',A8,' : ',8(F10.4,2X))
243    FORMAT('  MEAN WIDEPTH ',A8,' : ',8(F10.4,2X))
155    FORMAT('  C STORAGE ON ',A8,' : ',8(F10.4,2X))
150    FORMAT('  NETCFLOW ON  ',A8,' : ',8(F10.4,2X))
151    FORMAT('  AVGCFLOW OVER PERIOD  : ',8(F10.4,2X))
152    FORMAT('  DELTA CSTORAGE (mg)   : ',8(F10.4,2X))
153    FORMAT('  PRED DELTA CSTORAGE   : ',8(F10.4,2X))
154    FORMAT('  ERROR IN CSTORAGE     : ',8(F10.4,2X))
177    FORMAT('  ERROR IN WSTORAGE (%) : ',8(F10.4,2X))
178    FORMAT('  ERROR IN CSTORAGE (%) : ',8(F10.4,2X))
436    FORMAT(/,'  TOT ERROR IN WSTORAGE : ',8(F10.4,2X))
437    FORMAT('  TOT ERROR IN CSTORAGE : ',8(F10.4,2X))
438    FORMAT('  TOT ERROR IN WSTORAGE : ',8(F10.4,2X),/)
721    FORMAT(6A12)
       END
```

Table C.2. Sample output from program FLUX.

```
    COMMENT  : OPTIMIZING CONDUCTIVITY IN SUBAREA #1
    COMMENT  : USING PRZM PERCOLATION FLUX DATA
    PROGRAM RUN ON 04/22/1988  AT 10.43.20.59
    HYD COND. : 12.00  12.00  12.00  12.00  12.00  12.00  12.00
    POROSITY  :  .36
    X-NODE BOUNDARIES :   6 18
    Y-NODE BOUNDARIES :   2  8 14 18 22 26 30

DAYS SINCE APPLICATION: 40, PERCOLATION SINCE 12/15/86 =  1.32 cm
DELTA WSTORAGE (m^3)  :   -13.3543    -12.5565    -10.1853    -15.0013    -12.6839     -5.3586    -69.1410
PRED DELTA WSTORAGE   :    -3.3449      7.2061     -7.6461     21.0692    -15.0421     25.8956     28.1378

DAYS SINCE APPLICATION: 47, PERCOLATION SINCE 12/22/86 =  3.04 cm
DELTA WSTORAGE (m^3)  :     -.6429      -.4067      1.9388       .0304     -3.4596     -4.6639     -7.2030
PRED DELTA WSTORAGE   :    10.8180     16.7252      3.9850     33.0902    -13.0865     29.6292     81.1611

DAYS SINCE APPLICATION: 54, PERCOLATION SINCE 12/29/86 =  2.62 cm
DELTA WSTORAGE (m^3)  :    -8.7798    -12.0053     -6.6799     -5.3921     -5.2577     -5.5686    -43.6831
PRED DELTA WSTORAGE   :    10.1124     13.0013      3.2031     30.8369    -12.3547     26.2670     71.0661

DAYS SINCE APPLICATION: 61, PERCOLATION SINCE  1/05/87 =  2.75 cm
DELTA WSTORAGE (m^3)  :      .1695       .1741       .4625       .1102     -3.9066     -5.5415     -8.5320
PRED DELTA WSTORAGE   :    12.8376     13.5732      6.0237     27.4354     -4.5690     21.0263     76.3270

DAYS SINCE APPLICATION: 68, PERCOLATION SINCE  1/12/87 =  5.28 cm
DELTA WSTORAGE (m^3)  :     4.3478      5.5865      4.6180      3.6360      2.4435      2.5201     23.1521
PRED DELTA WSTORAGE   :    28.8188     31.1019     13.3882     44.5662     10.9241     31.1496    159.9487
```

Table C.2. Continued.

DAYS SINCE APPLICATION:174, PERCOLATION SINCE 5/03/87 = 1.41 cm							
DELTA WSTORAGE (m^3) :	10.9312	29.1446	7.8003	12.2948	16.2689	15.6362	92.0759
PRED DELTA WSTORAGE :	5.4211	10.4245	-2.4286	13.6757	7.6882	15.4218	50.2027
DAYS SINCE APPLICATION:177, PERCOLATION SINCE 5/05/87 = .00 cm							
DELTA WSTORAGE (m^3) :	-7.2057	-3.5609	-.2990	.2405	9.0190	16.4747	14.6681
PRED DELTA WSTORAGE :	-5.7125	-2.0040	-12.0272	8.0393	.3808	11.0193	-.3043
DAYS SINCE APPLICATION:182, PERCOLATION SINCE 5/08/87 = 7.54 cm							
DELTA WSTORAGE (m^3) :	15.6433	16.1147	4.6156	-.0760	-7.6467	-9.7187	18.9330
PRED DELTA WSTORAGE :	40.1281	46.0137	13.9722	50.9695	28.3841	51.0628	230.5303
DAYS SINCE APPLICATION:187, PERCOLATION SINCE 5/13/87 = .64 cm							
DELTA WSTORAGE (m^3) :	-21.3326	-20.2321	-12.0260	-9.1887	.8297	1.8801	-60.0701
PRED DELTA WSTORAGE :	-4.7329	1.1261	-11.7398	12.8980	-4.4958	23.3991	16.4547
DAYS SINCE APPLICATION:194, PERCOLATION SINCE 5/18/87 = .73 cm							
DELTA WSTORAGE (m^3) :	-14.5931	-23.8722	-15.4708	-22.5782	-24.5092	-15.6859	-116.7080
PRED DELTA WSTORAGE :	-2.6033	-1.1742	-6.8849	13.6701	-22.8199	29.7160	9.9038
DAYS SINCE APPLICATION:201, PERCOLATION SINCE 5/25/87 = .00 cm							
DELTA WSTORAGE (m^3) :	-5.4107	-10.3354	-4.0324	-3.4908	-9.9932	-14.0623	-47.3250
PRED DELTA WSTORAGE :	-5.2955	-5.4908	-4.8896	14.2750	-22.6561	13.5992	-10.4578
TOT ERROR IN WSTORAGE :	271.1864	338.8987	71.6449	620.3365	-97.0587	568.4956	1773.5030

APPENDIX D

SURFACE PLOTS OF ATRAZINE CONCENTRATION IN GROUNDWATER

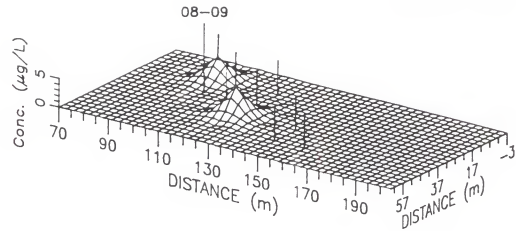

Figure D.1. Atrazine concentration in the groundwater on 1/19/87. Vertical bars indicate sampling locations.

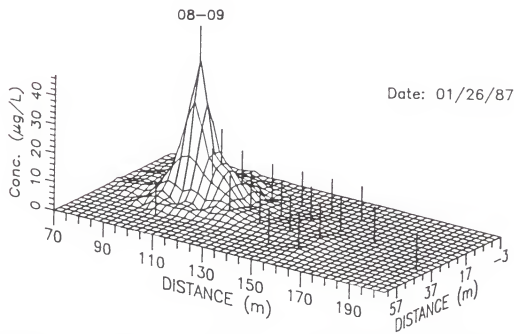

Figure D.2. Atrazine concentration in the groundwater on 1/26/87. Vertical bars indicate sampling locations.

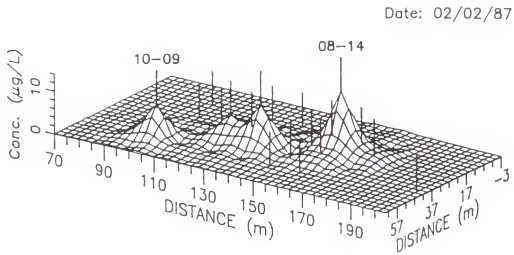

Figure D.3. Atrazine concentration in the groundwater on 2/02/87. Vertical bars indicate sampling locations.

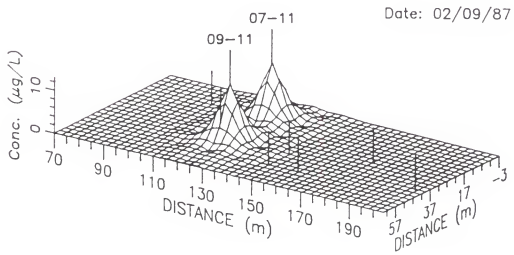

Figure D.4. Atrazine concentration in the groundwater on 2/09/87. Vertical bars indicate sampling locations.

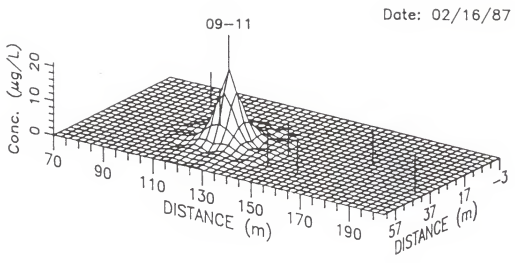

Figure D.5. Atrazine concentration in the groundwater on 2/16/87. Vertical bars indicate sampling locations.

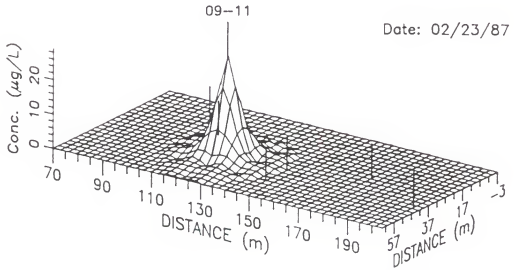

Figure D.6. Atrazine concentration in the groundwater on 2/23/87. Vertical bars indicate sampling locations.

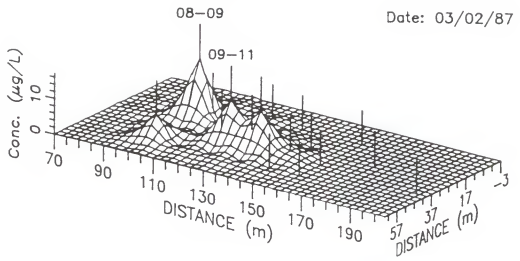

Figure D.7. Atrazine concentration in the groundwater on 3/02/87. Vertical bars indicate sampling locations.

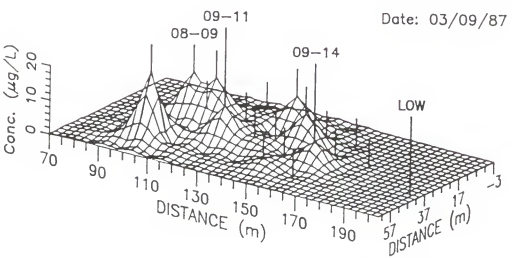

Figure D.8. Atrazine concentration in the groundwater on 3/09/87. Vertical bars indicate sampling locations.

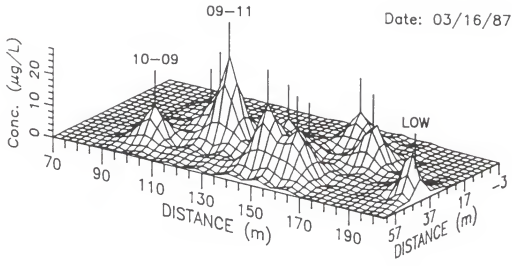

Figure D.9. Atrazine concentration in the groundwater on 3/16/87. Vertical bars indicate sampling locations.

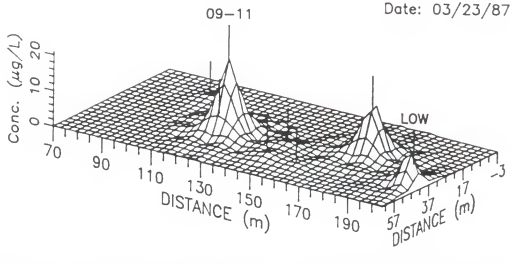

Figure D.10. Atrazine concentration in the groundwater on 3/23/87. Vertical bars indicate sampling locations.

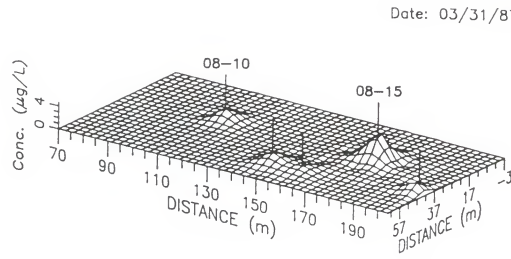

Figure D.11. Atrazine concentration in the groundwater on 3/31/87. Vertical bars indicate sampling locations.

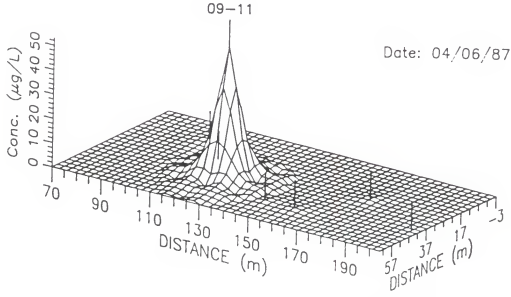

Figure D.12. Atrazine concentration in the groundwater on 4/06/87. Vertical bars indicate sampling locations.

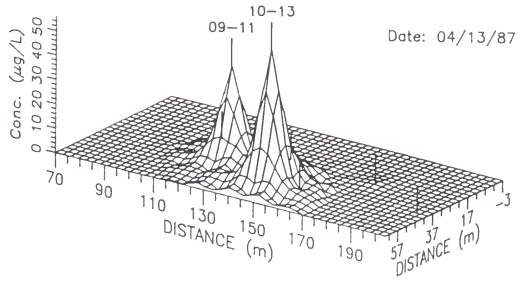

Figure D.13. Atrazine concentration in the groundwater on 4/13/87. Vertical bars indicate sampling locations.

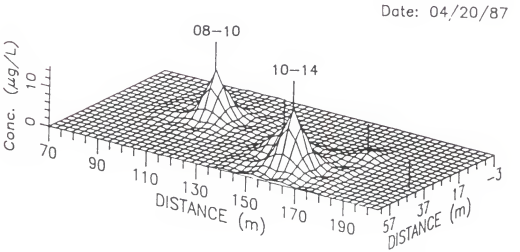

Figure D.14. Atrazine concentration in the groundwater on 4/20/87. Vertical bars indicate sampling locations.

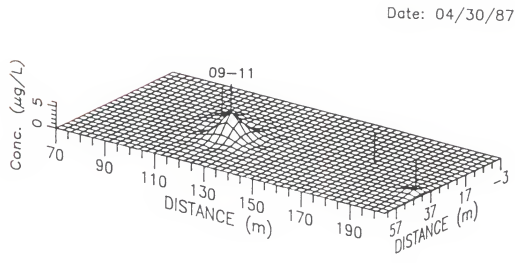

Figure D.15. Atrazine concentration in the groundwater on 4/30/87. Vertical bars indicate sampling locations.

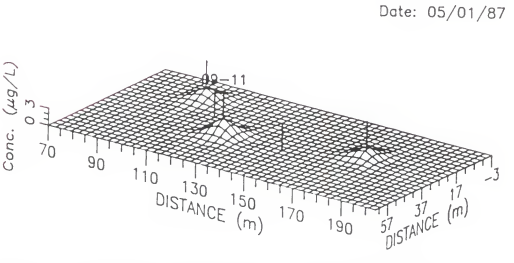

Figure D.16. Atrazine concentration in the groundwater on 5/01/87. Vertical bars indicate sampling locations.

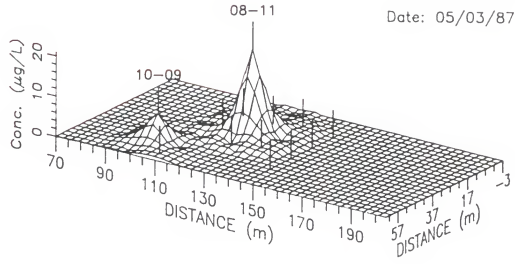

Figure D.17. Atrazine concentration in the groundwater on 5/03/87. Vertical bars indicate sampling locations.

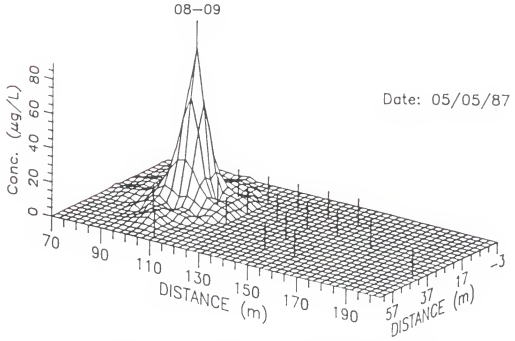

Figure D.18. Atrazine concentration in the groundwater on 5/05/87. Vertical bars indicate sampling locations.

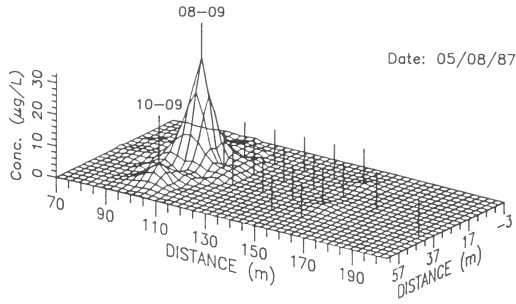

Figure D.19. Atrazine concentration in the groundwater on 5/08/87. Vertical bars indicate sampling locations.

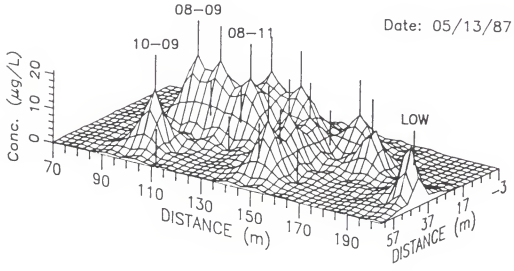

Figure D.20. Atrazine concentration in the groundwater on 5/13/87. Vertical bars indicate sampling locations.

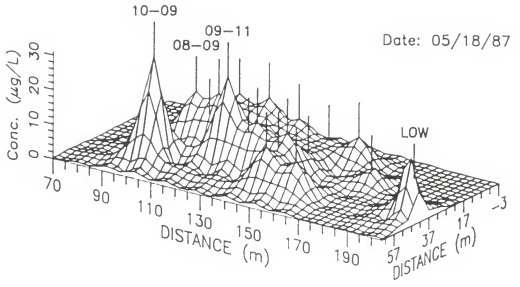

Figure D.21. Atrazine concentration in the groundwater on 5/18/87. Vertical bars indicate sampling locations.

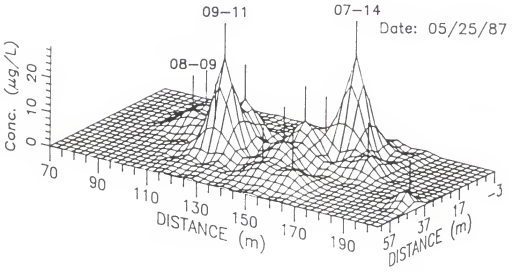

Figure D.22. Atrazine concentration in the groundwater on 5/25/87. Vertical bars indicate sampling locations.

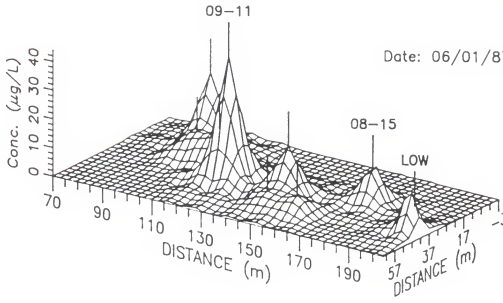

Figure D.23. Atrazine concentration in the groundwater on 6/01/87. Vertical bars indicate sampling locations.

BIOGRAPHICAL SKETCH

Matthew Clay Smith was born on September 27, 1957, in DeLand, Florida. He attended Deland Senior High School during 1973 and 1974. In 1974 he attended Brevard College in Brevard, North Carolina, under the early admissions program. In 1977 he received the Associate of Science degree from Abraham Baldwin Agricultural College in Tifton, Georgia. In 1980 he received the Bachelor of Science degree in agricultural engineering from the University of Georgia in Athens, Georgia. While attending the University of Georgia he participated in the cooperative education program by alternating quarters between academic courses and employment with the U. S. Environmental Protection Agency in Athens, Georgia.

He attended graduate school at North Carolina State University in Raleigh, North Carolina, where he worked as a research assistant in the Department of Biological and Agricultural Engineering. He received the Master of Science degree in 1983. His thesis topic was a study of the water and energy use efficiency of drainage/subirrigation systems.

He worked as a research agricultural engineer in the Department of Agricultural Engineering, University of Georgia, Coastal Plain Experiment Station in Tifton, Georgia, from 1982 to 1984.

He attended the University of Florida in Gainesville, Florida, where he worked as a research assistant in the Agricultural Engineering Department from May, 1984, through September, 1987.

In October, 1987, he began employment with the University of Georgia, Coastal Plain Experiment Station in Tifton, Georgia, where he holds the title of Assistant Professor in the Department of Agricultural Engineering.

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

A. B. (Del) Bottcher, Chairman
Professor of Agricultural Engineering

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

Kenneth L. Campbell, Cochairman
Associate Professor of Agricultural Engineering

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

Wayne C. Huber
Professor of Environmental Engineering Sciences

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

P. S. C. Rao
Professor of Soil Science

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

E. Dale Threadgill
Professor and Division Chairman
Agricultural Engineering, University of Georgia

This dissertation was submitted to the Graduate Faculty of the College of Engineering and to the Graduate School and was accepted as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

December, 1988

Dean, College of Engineering

Dean, Graduate School